5-1-1965

The Relationship Between the Viscosity and the De-Conductivity in Polyvinylchlorid UARI Research Report No. 20

Juerg-Heinrich Kallweit
THE RELATIONSHIP BETWEEN THE VISCOSITY AND THE DC-CONDUCTIVITY IN POLYVINYLCHLORID

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This research was supported partially by the National Aeronautics and Space Administration
Grant NsG-381

UNIVERSITY OF ALABAMA RESEARCH INSTITUTE
HUNTSVILLE, ALABAMA

March 1965
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Problem

It is common assumption that the dc-conductivity $\sigma$ in high-
polymers mainly depends on the sample viscosity $\eta$ because both the 
viscosity and conductivity show a similar strong temperature depen-
dence. In accordance with Waldens' rule, it is written

\[ \sigma \sim \frac{1}{\eta} \]

To check this relation, the same samples of Polyvinylchlorid (PVC) 
with varied plasticizer content (Palatinol AH = Dioctylphthalate) 
were used to measure the viscosity and dc-conductivity as function 
of time and temperature.

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**Research Institute, University of Alabama, P. O. Box 1247, Huntsville, 
Alabama.
PART I

Experiments

Samples with a thickness of 0.06 cm were cut from the following material:

Table I

<table>
<thead>
<tr>
<th>Sample No. and Symbol</th>
<th>PVC Vinoflex 332 Percent by weight</th>
<th>Plasticizer Palatinol AH + 0.5% Stabilizator Percent by weight</th>
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<tr>
<td>C +</td>
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<td>16</td>
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<tr>
<td>D •</td>
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<td>26</td>
</tr>
<tr>
<td>E ○</td>
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<td>37</td>
</tr>
<tr>
<td>F ▽</td>
<td>50</td>
<td>50</td>
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</table>

The viscosity $\eta$ was obtained from the results of a creep experiment. The measurements were done in accordance with the experiment described by Becker in [11]. A rod-shaped sample was fixed at the upper end in perpendicular position and charged with a load at the time $t = 0$. For small deformations, a tensile strength $s_0$ results, which is constant with respect to time. The relative change in the sample length $\varepsilon(t)$ was measured as function of time. The differentiation of the compliance $J$ with respect to the time

\[ J(t) = \frac{\varepsilon(t)}{s_0} \]

\[ \frac{dJ}{dt} = \frac{d\varepsilon}{dt} \frac{1}{s_0} = \frac{1}{\eta} \]

gives formally the equation for Newton's flow

\[ s_0 = \eta(t) \frac{d\varepsilon}{dt} \]
\( \eta(t) \) can be called also the Trouton-viscosity of the sample \( [2] \). \( [3] \)
can be written
\[
\frac{1}{\eta} = -\frac{d}{t} \left( \frac{1}{\eta} \right)
\]
The differentiation was obtained by graphical methods. From equation \( [3] \) follows that \( \eta \) must be a function of the time. The viscosity of high-polymers can be considered to be a criterion for the "friction force" between the position-changing segments of the molecular chains during stress. The decreasing possibility for position changes in stress direction leads to increasing the viscosity as function of the load period. To eliminate this time dependence as well as possible, only the \( \eta \)-values obtained three seconds after load charging were used for the comparison with the values of the specific dc-conductivity. Figure I shows the temperature dependence of the viscosity obtained after three with the plasticizer content as parameter.

The experimental device for the determination of the specific dc-conductivity is described in \([3]\). The samples were again placed in vacuum of about \( 10^{-4} \) Torr during the measurement. The applied voltage of 1000 volt was identical with an electrical field strength of 16.7 \( [\text{kV/cm}] \) All samples were heat treated, before each change of the measuring temperature, for one hour at a temperature 30\(^\circ\)C above the respective second-order transition temperature. Afterwards they were cooled down slowly (or heated up slowly) until the desired sample temperature was reached. This procedure was necessary to eliminate all polarization effects in the sample due to former charging. Polarization effects are the reason for the strong time dependence of the conductivity in
highpolymers. Unfortunately, it is not possible by the reason of the time constant of the experimental device to measure very high resistances after three seconds after voltage application. These values were needed for the comparison with the viscosity values obtained after three seconds. By this reason the measured values for $\sigma$ as function of time were graphically extrapolated to the time three seconds. The error in $\sigma$ due to the extrapolation is in all cases smaller than the error which would be obtained by using the $\sigma$-values after the time of the time constant of the device. Figure II shows the polarization voltage $P$ as function of temperature with the plasticizer content as parameter. The charging period was six hundred seconds [4]. The increasing of $P$ at higher temperatures and plasticizer contents is due to electrophoresis as it was proved by Wuerstlin [5]. The specific dc-conductivity, converted to CGS-Units for better comparison with the viscosity values, is shown in Figure III. The plasticizer content is again a parameter in the plot of $\lg \sigma$ as a function of inverse temperature.

The supposed relationship $\sigma \sim \frac{1}{\eta}$ follows from a simple model for the conductivity process. An ion with the unit charge of $q$ is moving through the sample under the force of an electrical field $\vec{E}$ with constant velocity $\vec{v}$; when in the equilibrium state, the electrical force of $\vec{E}$ is equal to the friction force of $\vec{F}$:

$$q \vec{E} = \vec{F} = f \vec{v}$$

(6)

In the one-dimensional case, the velocity $\vec{v}$ can be considered to be identical with the mean drift velocity $\bar{v}$ in direction to the field $E$. 
With Stoke's law for the factor $f$

(7) $f = 6 \cdot r \cdot \pi \cdot \eta$  \hspace{1cm} r = radius of the ion with supposed spherical shape

and

(8) $\sigma = Z \cdot q \cdot c \left( \frac{V}{E} \right)$  \hspace{1cm} c = concentration

$\eta = \text{charge unit}$

$Z = \text{valency; } Z \text{ is supposed to be } 1 \text{ in this paper}$

follows

(9) $\sigma (T) \cdot \eta (T) = \frac{q^2}{6 \pi r} \cdot c(T)$

$= \text{const} \cdot c(T)$

Because $\sigma$ also contains the temperature-dependent concentration $c(T)$, the product $\sigma \cdot \eta$ should be temperature independent. Figure IV shows that the expected relationship was not observed at all. There are two possible explanations: (1) Stoke's law is a too rough approximation in the case of the tested highpolymers; (2) The viscosity in Stoke's law is not identical with the viscosity $\eta$ obtained by retardation experiments, which may be called "macroviscosity." But an effective local viscosity $\eta'$ (microviscosity) must be used in connection with Stoke's law. Only in the case of fluids $\eta$ is a good approximation for $\eta'$.

At first it was necessary to check whether or not any relationship between $\sigma$ and $\eta$ could be found. It is known from dielectric measurements on PVC [6] that the maximum of the loss tangent was always nearly the same when the viscosity $\eta$ of the sample is the same given value. It made no difference whether the magnitude of $\eta$ was due to the temperature or whether it was due to the plasticizer used. Therefore, it was checked as to which relationship between $\sigma$ and $\eta$ exists
when equal magnitudes of $\sigma$ are considered, which can be due to temperature or due to plasticizer variation. The shape of the plot of $\log \sigma$ over $\log \eta$ seemed to indicate a hyperbola (Figure V). Afterwards, $\log \eta$ was plotted as function of the product $\log (\sigma \cdot \eta)$. The graphic representation (Figure VI) gives the desired possibility for the derivation of the relationship between $\sigma$ and $\eta$.

\[
\log \eta = m \log \sigma \cdot \eta + \text{const.}
\]

or

\[
\frac{m-1}{m} \sigma \cdot \eta^m = \text{const.}
\]

for the samples A, B, and C. The tan of the slope angle $m$ must be derived with the help of the above plot.

**PART II**

**Discussion**

The experimental results described in Part I seemed to show that it is problematic to use the viscosity values obtained by retardation experiments in connection with Stoke's formula in (7). It was asked which results would be formally obtained when the magnitude of the viscosity in formula (11) would be considered to be the magnitude of the effective local viscosity $\eta'$.

\[
\left| \eta^{m-1/m} \right| = \left| \eta' \right|
\]

$\eta'$ should have the dimension of a viscosity. The numerical results are given in Table II. Because $m$ is nearly one, the values for $\eta'$ are unexpectedly low; but it has been shown by Ferry [7] that the
order of the effective local viscosity for small foreign molecules may be of the calculated order. It is furthermore interesting to note that the compensation law \[8\] \[9\] seems to hold for the conductivity process in the system PVC/Plasticizer. (See Figure VII). Formula \(7\), written now as

\[
f = 6 \cdot \pi \cdot r \cdot \eta'
\]

would give for the equation in \(9\)

\[
\sigma(T) \quad \eta'(T) = \frac{2}{6 \cdot \pi \cdot r} \cdot c(T)
\]

The graph in Figure VIII shows that now the expected relationship is obtained. This result indicated continuation of the formal test by writing for the median drift velocity \(v\)

\[
\bar{v} = \frac{q \cdot E}{6 \cdot \pi \cdot r \cdot \eta'}
\]

and for the conductivity

\[
\sigma = c \left( \frac{2}{6 \cdot \pi \cdot r \cdot \eta'} \right) / \text{valency } z = 1
\]

where the mobility \(b_e\) of the ions is given by

\[
b_e = \frac{q}{6 \cdot \pi \cdot r \cdot \eta'}
\]

Finally, the expression for the diffusion coefficient \(D\) would be

\[
D = \frac{KT}{6 \cdot \pi \cdot r \cdot \eta'}
\]

because the relationship between the electrical and mechanical definition for the mobility is \(b_e = q \cdot b_{\text{mech}}\). Table III gives the numerical results for the samples A, B, C and some values for \(D\). The calculation could not be done without another assumption for the radius \(r\) of the ions. The kind of the ions is not known, but most probably they will be small molecules. Under this assumption, two possible values were
chosen for the unknown radius $r$:

$r = 1 \cdot 10^{-7}$ cm

$r = 5 \cdot 10^{-7}$ cm

The values for sample D were added to show that the nonlinear plots in Figure VI do not give sensible values.

The crude approximations do not allow detailed discussion of the result summarized in Table III. But this result seems to indicate that the values for the ion velocity, concentration, and the diffusion coefficient are of a range, which could be a more-or-less fair approximation of the actual values. The expected temperature dependence of the mobility of the single samples was obtained. But it is difficult to understand that the mobility did not increase with increasing plasticizer content.

The common assumption is that the increase of the conductivity with higher plasticizer content is chiefly due to the greater ion mobility. Here it would turn out that the ion concentration is the dominating factor. The values for the diffusion coefficient do not differ markedly from the values of Luther and Meyer, who measured the diffusion coefficient of plasticizer in PVC \cite{10}. For sample C at 343°K was measured $b = 1.2 \cdot 10^{-10}$ $\text{cm}^2 \text{sec}^{-1}$ and by Meyer $D = 1.4 \cdot 10^{-11}$ $\text{cm}^2 \text{sec}^{-1}$.

Although it cannot be said that plasticizer molecules are responsible for the charge transport, the low order of the diffusion coefficient may indicate that molecules as charge carriers are migrating under the force of the applied electrical field.

The calculated values for $D$ and $\bar{v}$ can be used to check whether or not values are obtained for the jump distance $d$ of the ions, which
are of the same order as values known from literature. Foss and Danhauser \[11\] evaluated the jump distance in PPN according to the reaction rate theory from the isothermal field dependence as about 200 Å; Amborski \[12\]
measured for Mylar at 130° C, 69 Å. The values in the case of PVC without plasticizer would be for the assumed ion radius \( r = 1 \cdot 10^{-7} \) Å, identical to 127 Å (See \[12\]); but this fair agreement should not be overvalued because \( D = \bar{v}d \) turns out, according to the approximations used in this paper, to be independent from any specific sample.

Other types of highpolymer material must be tested before any statements can be made. The determination of the free volume should be added to the viscosity measurements, and the dc-conductivity should be measured as function of temperature and electric field strength \[17\]. Samples with varied plasticizer content and crystallinity should be checked. The understanding of the dc-conductivity in highpolymers depends on the exact knowledge of the mobility of the charge carriers.
ACKNOWLEDGEMENT

The author would like to thank Dr. G. W. Becker, Physikalisch-Technische Bundesanstalt, Braunschweig, Germany, for the measurement of the viscosity and for many valuable discussions.

The samples are courtesy of Dr. Wuerstlin, Badische Anilin und Sodafabrik, Ludwigshafen, Germany.

The experiments were done in the Physikalisches Institut, Technische Hochschule, Braunschweig, Germany. I would like to thank the director, Professor Dr. Cario.

This was partially funded by the National Aeronautics and Space Administration under NsG-381.
REFERENCES

In general, it has been said that the dc-conductivity $\sigma$ is proportional to the inverse viscosity $\eta$. But the relation $\sigma \cdot \eta = \text{const}$ has not been proven in the case of the system Polyvinylchlorid/Dioctylphthalat. The experimental results can be described by $\sigma \cdot \eta^{m-1} = \text{const}$ if the plasticizer content is not too high. The ion mobility seems to depend on a local effective viscosity, which differs from that viscosity which is derived from retardation experiments.
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<th>η</th>
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**TABLE II**
CAPTIONS TO FIGURES

Figure I:
Log Viscosity Vs. Reciprocal Temperature For the System PVC/DOP. The Plasticizer Content Is Parameter.

Figure II:
The Polarization Voltage as Function of Temperature. The Plasticizer Content Is Parameter; Charging Time Is 600 Seconds.

Figure III:
Log Specific Conductivity Vs. Reciprocal Temperature For the System PVC/DOP. The Plasticizer Content Is Parameter.

Figure IV:
Log (Specific Conductivity Times Viscosity) Vs. Temperature.

Figure V:
Log Specific Conductivity Vs. Log Viscosity.

Figure VI:
Log Viscosity Vs. Log (Specific Conductivity Times Viscosity) With the Plasticizer Content as Parameter.

Figure VII:
Log (Specific Resistance) Vs. Activation Energy.

Figure VIII:
Log Specific (Conductivity Times Effective Viscosity) Vs. Temperature.
The Relationship Between The Viscosity And The DC Conductivity In Polyvinylchlorid

UARI Research Report No. 20

Huntsville, Research Inst. March '65

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