wonder whether an explanation of the size effect offered by you, might also be applied to the case of the filled systems investigated by us?

A. J. Kovacs (Strasbourg): I think that carbon-black and NaCl interact differently with the surrounding rubber layer, the adsorption on the first one being much stronger than on the crystallic surface of NaCl. The thickness of the "glassy" layer adsorbed depends probably on the ratio of rubber-rubber and rubber-filler interaction.

G. Rehage (Aachen): Ich möchte die Bemerkung von Herrn Dr. Kovacs unterstützen, daß sich zwischen den Rußteilchen und dem umgebenden Kautschuk starke Bindungen einstellen. Wenn man einen aktiven Füllstoff in genügend hoher Menge in ein unvernetztes Polymerisat gibt, löst sich das Polymerisat nicht mehr in einem Lösungsmittel auf, sondern quillt nur noch wenig. Das ist ein Zeichen dafür, daß die Rußteilchen Vernetzungstellen gebildet haben.

P. P. A. Smit (Delft): It is well known that carbon black has a sufficient number of radical acceptor sites, about 2.10^{18} per m² for HAF, which if all reacted with the rubber could lead to a high cross-link density at the surface. However, from swelling experiments on un Vulcanised rubber only a relatively low number, leading to a slight crosslinking at the surface, can be deduced to be effective. Moreover, if one swells the rubber in a sufficiently good solvent at elevated temperatures, the rubber-carbon gel dissolves, so the nature of the rubber-carbon link is not defined unambiguously as being chemical. In order to account for the phenomena discussed here crosslink density at the surface must be very high and nothing known from the literature points in this direction, but most evidence can be explained by concepts of adsorption of the rubber on the black surface, though chemical reactions may contribute as well.


Hier sind die Moleküle in den Kristallen fest einge- baut. Dies könnte ein Hinweis auf die Festigkeit der Adsorption der Kautschukmoleküle an den Ruß sein.

M. Van den Tempel (Vlaardingen): The effect of a filler on mechanical properties can always be explained by (1) an adsorbed layer of different properties, or (2) interaction between filler particles, such as by van der Waals forces. The real problem is here to find a decisive experiment that can distinguish between the two; this has only been done for aqueous systems where no change in mechanical properties was found up to a few Å from the surface. It might be possible that polymer molecules can feel the presence of a surface even at a distance of up to 10 or 20 Å, but any more quantitative theory of this effect should in any case account for the presence of interaction, which appears to be always present and might well explain all or most of the effects considered.

P. P. A. Smit (Delft): Of course if one has to treat more quantitatively the problem one has to take also into consideration the possibility of solid-solid interaction. However, both from our work and also the work of Payne one point, which is mostly neglected, makes it very unlikely that solid-solid interaction is the predominant effect in the case of rubber carbon black vulcanisates. As the dependence of the modulus at low deformation amplitudes indicates that at high temperatures the influence of rubber-filler or filler-filler interaction disappears. As the Van der Waals forces must be considered to a great extent to be temperature independent in this temperature region, it does not seem appropriate to explain the high modulus of carbon-black-filled vulcanisates by filler-filler interaction.

1. Introduction

The glass-rubber transition is a phenomenon which is very generally observed in high polymers. Clearly is it occurrence does not depend on structural details of the polymer molecules. Moreover, in non polymers glass-liquid transitions are found resembling the glass-rubber transitions of polymers, so the phenomenon is not restricted to polymers.

Since the phenomenon is so general one may hope to describe it by a very general model. Once the model is shown to be generally applicable one can measure sufficient quantities to calculate the characteristic parameters of the model. These may then either be used to predict the macroscopic behaviour of the material under a variety of conditions or they can be related to properties of the molecules responsible for the transition.

The envisaged model can be "molecular" or "kinetic" or "thermodynamic", in which order the generality increases at the same time as the detailed information supplied by it decreases. Sometimes and also in our case from a careful study of the thermodynamic model information on the kinetics or the molecular mechanism can be derived.
2. Ehrenfest's Transitions

A thermodynamical model of the glass-rubber transition which has been used, discussed and rejected frequently in the literature is Ehrenfest's second order transition (1). Ehrenfest's generalisation was more of a mathematical than of a physical nature and it has turned out that transitions found experimentally sometimes cannot be easily classified according to this scheme. Yet one fundamental idea of Ehrenfest was sound: whenever a "transition" occurs certain thermodynamic quantities or derivatives pass through a discontinuity and quantitative relations may or may not exist between the magnitude of those discontinuities. From the existence of such relations conclusions may be drawn about certain aspects of the mechanism involved in the transition.

Ehrenfest started by considering the well known phase transitions like melting, evaporation and condensation, which he called first order transitions. For these transitions we know that in the transition point the Gibbs free energy of the two phases is equal

\[ G' = G'' \]  

but the derivatives of \( G \) with respect to \( p \) and \( T \) are not equal;

\[
\left( \frac{\partial G'}{\partial T} \right)_p = -S', \left( \frac{\partial G'}{\partial p} \right)_T = V' \quad \text{and} \quad \left( \frac{\partial G''}{\partial T} \right)_p = -S'', \left( \frac{\partial G''}{\partial p} \right)_T = V''
\]

\[ \Delta S = S'' - S' \]
\[ \Delta V = V'' - V'. \]

\( p, T, S \) and \( V \) have the usual meaning of pressure, temperature, entropy and volume.

Consequently the planes for \( G' \) and \( G'' \) in \( G-p-T \)-space intersect. The slope of the line of intersection \( \left( \frac{dp}{dT} \right)_{tr} \) can be calculated from the condition (1) which implies that along this line everywhere \( dG' = dG'' \) or

\[ \Delta V \frac{dp}{dT} = \Delta S \frac{dT}{dT} = 0 \quad \text{or} \quad \frac{dp}{dT} = \frac{\Delta S}{\Delta V} = \frac{AH}{T \Delta V} \]

the equation of Clausius-Clapeyron.

Then Ehrenfest defined second order transitions in which not only \( G' = G'' \) but also \( S' = S'' \) and \( V' = V'' \) while now the derivatives of \( S \) and \( V \) show a discontinuity.

Calling

\[ -\frac{\partial G}{\partial T^2} = \frac{\partial S}{\partial T} = \frac{C_p}{T} \]

with \( C_p \) specific heat

and

\[ -\frac{\partial G}{\partial p^2} = \frac{\partial V}{\partial p} = -\kappa V \]  

with \( \kappa \) the compressibility

we have now

\[ C_p'' - C_p' = \Delta C_p \]
\[ \kappa'' - \kappa' = \Delta \kappa \]
\[ \alpha'' - \alpha' = \Delta \alpha. \]

\[ \frac{dp}{dT} \]  

The transition line in \( G-T-p \)-space is now defined by three equations \( G' = G'', V' = V'' \) and \( S' = S'' \) from which one derives immediately

\[ \frac{dp}{dT} \]  

\[ \frac{\Delta C_p}{TV \Delta \alpha} \]  

\[ \frac{\Delta \alpha}{\Delta \alpha} \]

\[ \frac{\Delta S}{\Delta V} \]

and, of course

\[ \frac{\Delta C_p}{TV \Delta \alpha} = \frac{\Delta \alpha}{\Delta \alpha} \]  

\[ \frac{\Delta S}{\Delta V} \]

Thus we not only find two instead of one expression for the slope of the transition curve but also a relation between the magnitude of the jumps in \( C_p, \kappa \) and \( \alpha \) which should be generally valid.

Many experimentally observed transitions show a behaviour lying in between first and second order in Ehrenfest's sense and thus Ehrenfest's classification does not fit in very well with the experimental material.

With respect to the glass-rubber transition it should be clear from the start that this transition is not a second order transition in Ehrenfest's sense, because Ehrenfest considered states in equilibrium, that is having a minimum of free energy as compared to adjacent states. We know, however, that in the case of the glass-rubber transition the apparent stability of the glass state does not originate from having a minimum in free energy compared to adjacent states but from the circumstance that adjacent states cannot be reached for kinetic reasons. This is also shown by the time dependence of the transition.

One can, however, go one step further beyond stating that the transition is not a second order Ehrenfest transition and ask whether any of the equations [6] remains valid under certain conditions for this transition. That this might be so is seen on considering that the glass-rubber transition has important features in common with a second order Ehrenfest transition. At the transition point for the different states \( G' = G'', V' = V'' \), and \( S' = S'' \).

3. Internal Parameters

In the transitions envisaged by Ehrenfest only two "states" are important. At every \( p \)