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Simulation Calculations of the Charge Carrier Transport in Polyethylene

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Summary

The prerequisites for simulating the charge transport by MONTE CARLO methods are summarized and tested by experiment with PE. For this simulation calculations space charges have to be considered, particularly in interpreting the long-time kinetics. For them MONTE CARLO methods were found to be insufficient. In investigating the long-time kinetics by surface potential measurements deviations from the dispersive behaviour were observed.

Introduction

The time-dependent transport of charges and energy in disordered systems has become an object of intensive theoretical and experimental studies. Particularly in polymer solids a significant time-dependence of the direct current has been observed. An essential aspect of these investigations is the elucidation of basic problems combined with the electronic properties of polymers, especially with the charge transport processes and with the electronic structure. The current approaches of these processes play an important part in technical or commercial applications, even if they restrict the performance of the materials designed. These aspects are of consequence, for example, in

- electrophotography (transient photocurrent in polymers, PVK-TNF)
- electronics (charge drift in thin polymer films applied as charge storing materials or electrete transducers (PTFE, FEP))

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- electrical engineering (effects on the breakdown and the life-time characteristics of polymer insulators, PE).

This paper will be concerned only with the charge carrier transport in PE as an example of polymer insulators and consider the demands to be met in simulating the charge carrier transport in polymer insulators.

Our experimental studies suggests the charge transport process in PE to discuss by a hopping mechanism of injected excess electron charges over localized levels being localized within a broad gap (~ 7 eV) and energetically subjected to a GAUSSIAN distribution (BREHMER, PINNOW and BREHMER).

Dispersive transport and simulation calculations

For the first time by SCHER and MONTROLL a stochastic transport model was used for explaining the anomalous transient phenomena in disordered solids.

By considering the anomalous dispersion to be caused exclusively by variation of the spatial coordinates the SCHER and MONTROLL concept leads to the following expression for the current kinetics

$$j(t) \sim \begin{cases} t^{-(1-\alpha)} & \text{for } t < t_T \\ t^{-(1+\alpha)} & \text{for } t > t_T \end{cases}$$

Here, the current kinetics is characterized by superlinear field strength (E) and thickness (L) dependence of the transit time t_T, which, however, are correlated by the same disorder parameter α and thus lead to the universality principle with regard to E and L.

The non-GAUSSIAN dispersive transport proceeding by trap-limited multiple trapping has generally been accepted. However, the dispersive transport by hopping processes is less elucidated and thus the object of controverse interpretations. Summarizing the literature in this field (see MARSHALL and SHARP, SCHAFFMANN and SILVER, SILVER and DATTA, SCHÖNHERR et al.) we can state, that the hopping transport over sites having GAUSSIAN distribution of energy (as in PE) resulted in dispersive behaviour under defined conditions, too.

In spite of the recent progressive development of dispersive

transport theories the applicability of these purely theoretical approaches was tested by computer simulation based particularly on MONTE CARLO and cluster methods.

Testing of the prerequisites of simulation calculations with PE

MONTE CARLO methods were particularly applied successfully in simulating the hopping transport process. Here, the prerequisites of this approach have to be tested with respect to their validity for simulating the charge transport in polymer insulators (PE) under the conditions of operation. The MONTE CARLO methods are based essentially on the following assumptions:

1. Instantaneous injection of charge carriers or charge carrier packets is considered exclusively,
2. Any correlation and effect of the stochastic transport path of a charge carrier with or on other carriers is neglected, that is, any site in the suggested lattice is considered to be unoccupied,
3. Consequently, this means that the life-time of the trapped charge carriers is neglected and, thus, the formation of space charges characterized by long-time stability cannot be considered,
4. The small-signal case is considered only, that means all charge carriers are assumed to move in a system free of space charges,
5. The MONTE CARLO calculations are based on static diagonal disorder or off-diagonal disorder approaches,
6. Finally, the macroscopic inhomogeneities resulting in different distribution within different regions are not taken into consideration.

The first prerequisite is obviously not satisfied, because the injection process for insulating arrangements extends all over the operation period, that means as long as an electric field acts at the contacts of the sandwich arrangement.

Of particular importance in simulation calculation is the question whether or not space charges are formed and remain stable because the answer would involve serious consequences

with respect to the simulation approach applied. Therefore, this topic should be carefully discussed and elucidated by experimental investigations. In Fig. 1 the kinetics of the isothermal discharge current (IDC) is represented, with the

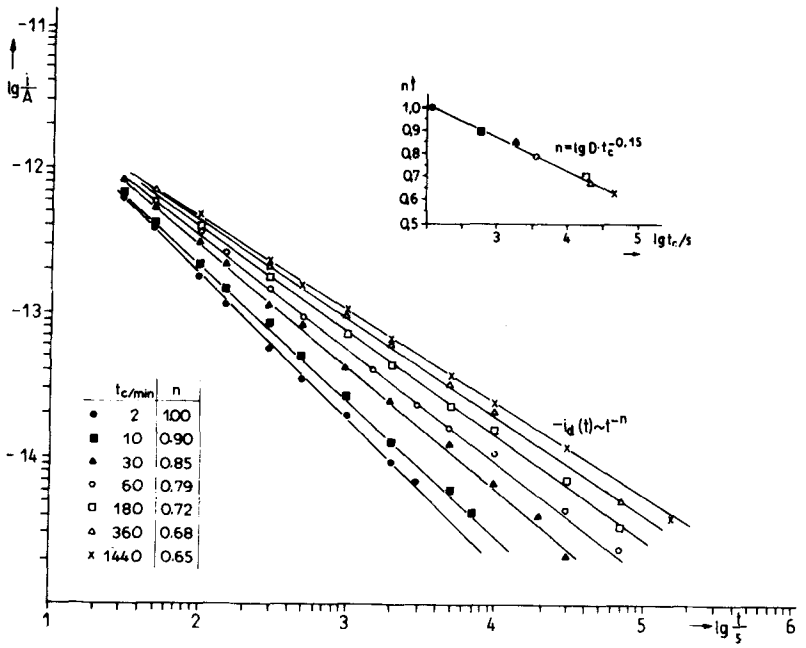

Fig. 1. Isothermal discharge current i_d (parameter: injection period t_c)

injection period t_c as parameter. Each series of measurement is affected by the space charges formed in the preceding experiment. Even at long injection and decay periods the formation of space charges has not come to an end. These experimental results illustrate the effect of the injection period on the behaviour of j(t) and on the long-time space charge formation as well. This long-time effect causes irreproducibility of the experimental results even if between the particular measurements the sample is under short-circuit conditions. The results are presented in Fig. 2 and demonstrate the extremely long-time stability of space charges. From these results the dc properties are expected to be principally irreproducible. This was attested also by applying the methods of current-voltage characteristics (CVC), surface potential kinetics V(t) and thermal stimulated currents (TSC).

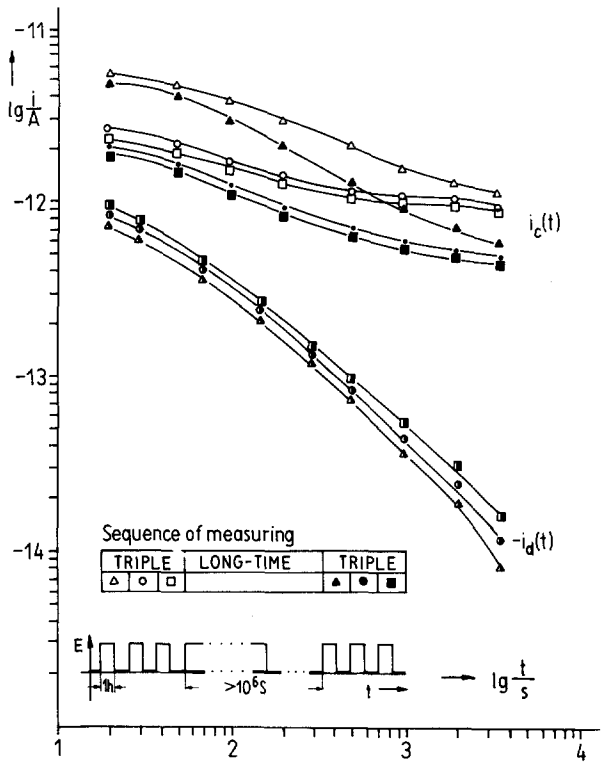

Fig. 2. Isothermal charge currents i_c and discharge currents i_d (T = 360 K)

Fig. 3 shows four current-voltage characteristics measured consecutively. Between measuring the particular characteristics the sample was under short-circuit conditions for 24 h. The characteristics are shifted parallel in the direction of lower currents, since a subsequent CVC reflects only additional space charges with respects to those formed in measuring the preceding CVC and does not express the overall space charges. The absence of changes of the molecular and supermolecular structure during the measurements was ascertained. These CVC characterized in detail by PINNOW and BREHMER are in accordance with a GAUSSIAN trap distribution with the parameters E_t = 0.7 eV and β = 0.05 calculated by a computer fitting programme (PINNOW and BREHMER).

As demonstrated in Fig. 4 also the surface potential kinetics after Corona charging shows systematic changes in repeating the charging-measuring cycles. Here the plots 2 to 7 rise subsequently to a higher level because the space charges add up analogous to the repeated measurements of charging and discharging currents.

Thus the experimental results suggest the formation and decay of space charges to be a long-time phenomenon (extend-

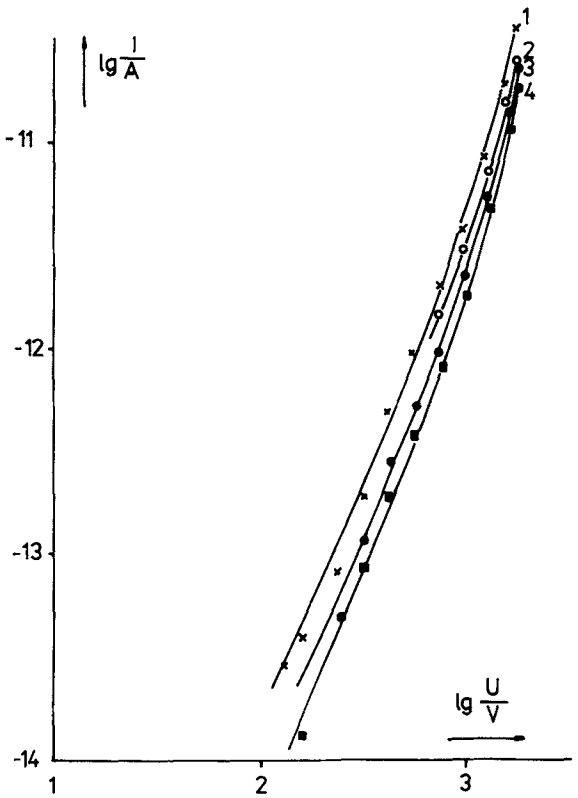

Fig. 3. Current-voltage characteristics CVC (1, 2, 3 and 4 measured consecutively, T = 383 K)

ing as a rule, essentially beyond the measuring time), which affects considerably the dc properties of PE. Even by annealing at temperatures about 10 K below the melting point the space charges cannot completely eliminated. Therefore, the existence and dynamics of space charges cannot be neglected in simulation calculations.

Furthermore, the space charge concentration estimated from TSC measurements was 3.10^{20} m^{-3}. This means that the space charge stored in the volume is higher than that caused by geometry and voltage applied and therefore the amount of space charges requires the large signal case to be considered.

A particularly sophisticate problem is the modelling of the defect structure of partially crystalline PE. An efficient approach to the structure requires the consideration of ordered regions (lamellae, spherulithes) and amorphous regions as well. Further, the interface between crystalline and amorphous regions caused additional deep traps. The crystalline and amorphous regions are characterized by different concentration and different energetic and spatial distributions of sites. Simulation calculations with parti-

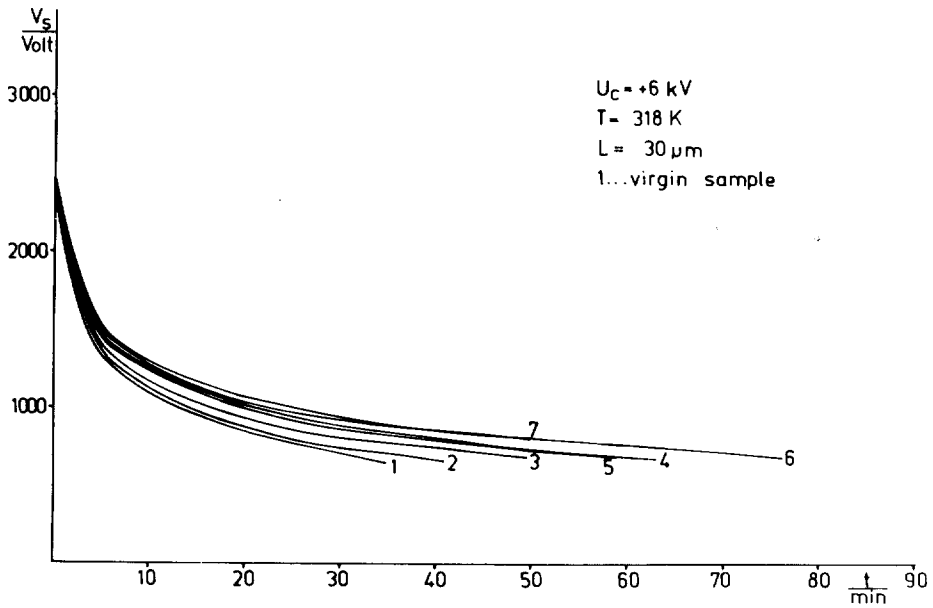

Fig. 4. Surface potential kinetics after Corona charging (1, 2...7 measured consecutively)

ally crystalline polymer systems should involve these inhomogeneities.

Additional with polymers not only the static diagonal disorder and off-diagonal disorder but also a dynamic disorder effect has to taken into consideration (DUKE). We suggest the dispersive transport not only to apply for the interpretation to the experimental results in short-time range but also to extend to long-time measurements. Obviously, the particularities mentioned above will be reflected in the dispersive long-time transport properties of PE and will lead to a modified transport properties. Thus, by measuring the surface potential after Corona charging the universality principle was not supported with the HDPE samples used in our experiments. Likewise, the dispersive transport cannot be described by only one dispersion parameter (BREHMER et al.), but the initial and final values are related by

$$0.7 = \alpha_i > \alpha_f \sim 0 \text{ for } T = 290 \text{ K.}$$

An inequation of this kind was established also already by PFISTER in TOF experiments with polycarbonates and by PERL-

MAN and BAMJI with PE. The inequality $\alpha_i \neq \alpha_f$ is suggested by PFISTER to be caused by space charges and surface effects. The difficulties arising from $\alpha \longrightarrow 0$ in our experiments have not been explained yet.
This behaviour in polymer insulators should be tested by simulation calculations. Simulation calculations of the charge transport in PE cannot be based on the prerequisites required for applying MONTE CARLO methods. The development of suitable simulation methods has to consider the results described above especially the space charges. In our opinion, this does not relate to PE only but also to other partially crystalline high-ohmic polymer solids characterized by low charge carrier mobility ($< 10^{-13} m^2 (Vs)^{-1}$). The charge carrier mobility in our HDPE samples was estimated by several techniques (BREHMER) to $10^{-14} m^2 (Vs)^{-1}$ for the slow mobility component. The formalism and the results of a computer programme for simulating the charge transport in PE taking into consideration essential features discussed above will be published elsewhere.

Conclusions

For better understanding of the charge carrier transport processes in polymer insulators simulation calculations were carried out. Until now these calculations have based first of all on MONTE CARLO methods neglecting the stable space charges. Our experimental results show that the space charges have to be taken into consideration for improved theories concerning polymer insulators, because the space charge and space charge dynamics influence the long-time electric properties of PE in an absolutely essential way. These effects have a great importance on the increasing application of PE as cable insulating material.

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