

Chapter 3

Conduction Mechanisms and Numerical Modeling of Transport in Organic Insulators: Trends and Perspectives

3.1. Introduction

Most of the physical concepts currently used to describe charge transport and breakdown in solid dielectrics have been known for over 20 years. With regard to polymers which are disordered materials, these concepts essentially stem from amorphous semiconductor physics [DIS 92] with the fundamental notions of *hopping* conduction, space-charge controlled current, interface states, etc. The dielectric nature of the media under consideration explains the references to the concept of the polaron [see Chapters 1 and 2; BLA 01] which describe the coupling between an electrical charge and its environment, or that of molecular charge states in polymers [DUK 78]. Some excellent review articles, among which some very recent, describe the basis of our current knowledge in this domain [LEW 02], [LEW 90], [WIN 90], [BLA 98], [WIN 99], [LEW 98], [MIZ 04], [BOG 05].

Despite this background in physical mechanisms, work on charge transport modeling has been rare over the course of the past 20 years. Most of the time, they have concerned analytical models in simple case studies or under very restrictive conditions when compared with real conditions of materials in electrical systems.

The difficulty for the development of such models has been the lack of basic data, such as the nature of carriers and traps, charge mobility and their local density, etc.

Furthermore, information on the microscopic process controlling charge transport was unavailable, simply because all the experimental measurements were based on techniques said to be “integral” which brought the information in time and/or in space (for example: surface potential measurement of a dielectric resulting from an internal distribution of charges).

Two developments have contributed to change the situation: the first is related to the tremendous increase of the calculating power of computers and to the development of numerical techniques [WIN 90]; the second concerns the development of experimental techniques which today allow the measurement of the internal distribution of the space charge as a function of time. The birth and the development of these measurement techniques in the course of the past 20 years unquestionably marks an important step in the dielectric domain. Several methods to measure the space charge have emerged, and have provided new information, principally on polymers [FLE 05], [SES 97], [TAK 99a,b], [BAU 03], [LEW 05]. Nowadays, these methods permit a range of information to be obtained, such as: the polarity of the carriers (although only the net charge is detected and we also measure the polarization gradients); the charge carriers mobility or the depth of the traps in different field and temperature situations. By combining the measurement techniques of the space charge with different spectroscopic methods such as luminescence experiments, more information can be obtained on the recombination processes which can indicate, for example, whether the transport is bipolar or unipolar [TEY 01a,b].

Another, cultural, factor has considerably changed the situation: research in the engineering sciences has been made in closer collaboration with manufacturers. Thus, this research has been made with a view to supplying a simple but realistic representation of physical, electrical and chemical phenomena, at the microscopic scale, so that it can be exploited in macroscopic models. Among the reasons which have provided an incentive to the development of models capable of describing the charge transport phenomena within insulating polymers under thermoelectrical stress, are:

- the evolution towards more and more compact systems in power electronics and, more generally, in all domains of electrical engineering, leading to an increase in power density (increasing voltage and current), with two consequences for polymeric insulations: first, these materials are continuously subjected to strong stresses, often close to the limits they can sustain; second, manufacturers have to develop new tools capable of making best estimates of the intrinsic limits of the insulator used, in order to guarantee the security of their installation;

– the demand for more and more reliable electrical systems, principally due to their use in critical applications (large-scale electrical networks, embedded networks, complex systems, etc.). This is why new predictive models capable of anticipating the consequences of chemical and/or physical defects need to be elaborated;

– the research of new materials for electrical insulation such as, for example, the composites with micro- or nano-metric size inorganic charges [TAN 05], with chemical functionalization (by addition or grafting) of the matrix or of the charges. The models must be sufficiently elaborated to fit these data.

Our objectives in this chapter are neither to inspect the published works on modeling nor to introduce new dielectric physical concepts. We aim to show that, considering the accumulated knowledge on the physics of transport, there is a real window of opportunity to further develop simulation activities, in order to better control the behavior of polymer insulators under electrical stress. The term “modeling” here is meant in the largest sense: some approaches can be based on microscopic concepts while others, according to the nature of the problem, will be based on macroscopic models. These approaches lead to different information and can be used for various reasons, contributing either to the understanding of the physics of dielectrics, or to new technological and/or industrial applications. We think that all the conditions are met – the computer tools, the understanding of physical phenomena, the development of experimental techniques – to develop transport and degradation models which integrate different levels of physical approaches. The objective of this chapter is to underline the important steps made over these past 20 years in transport simulation and to anticipate the trends for the following years.

The first part of the chapter concerns atomistic modeling which starts from atomic or molecular properties to build collective properties for combinations of such elementary components. On the basis of these models, band gap properties, trap levels, and the mobility of carriers have been defined. In the second part, a macroscopic approach is established so as to describe and analyse the different existing transport models. These models permit the simulation of the electrical response of a dielectric under stress. The second part also deals with macroscopic approaches: the electrical response is modeled using “effective” parameters which encompass microscopic phenomena without explicitly describing them (nor really controlling them). The last part of the chapter (section 3.4) presents trends and perspectives in this research field. Many microscopic processes are still poorly defined (interfaces, the impact of the structure on trapping), but the limiting step for progress is no longer of an experimental order: numerous experimental methods today allow space charges to be probed with a continuously improved resolution in time [FLE 05] and in space [STE 05].

Amongst insulating materials with a large band gap, polyethylene (PE) stands out by its simple chemical structure (repetitive unit CH_2), its chemical inertness, and its numerous applications in electrical engineering. Although this chapter is not exclusively devoted to polyethylene, we are forced to note that this material has been most often considered as a model for the fundamental studies (molecular descriptions, macroscopic modeling) which makes it by far the most studied material.

3.2. Molecular modeling applied to polymers

Molecular simulation techniques are used to predict materials properties resulting from their physical or chemical structure. Indeed, the individual properties of atoms or molecules allow collective phenomena, which develop by the physical or chemical bonding of these elements, to be understood. In the case of organic polymers, which have strong covalent bonds along the chain and weak inter-chain bonds (these being essentially caused by electrostatic forces, of the Van der Waals type, or of hydrogen in specific cases), different interaction levels must be considered. With regard to the properties of a unique isolated macromolecule, the elementary entities to consider are the monomer units. On the other hand, the properties of amorphous or crystalline domains are described exclusively if many segments of adjacent chains are considered. The techniques referenced in this section have been used from 1997 onwards to foresee the trapping properties of polyethylene (PE) and to relate molecular-scale defects to the formation of space charges [MEU 97], [MEU 98]. Molecular simulations involve both the ab-initio quantum method (Density Functional Theory (DFT)) and classical molecular dynamics techniques. DFT has really developed since 1964 by becoming an alternative to the usual quantum mechanics representations of the electronic state and by supplying more direct information of interest for chemists (electronegativity, rigidity, reactivity for example). It was used to solve the Schrödinger equation for systems comprising a high number of atoms, and to derive diverse electronic properties (such electron affinity) to which the trapping properties for a given molecule ensues. As for molecular dynamics, it has been used to generate states of metastable molecular conformation of *n*-alkanes chains ($\text{C}_n\text{H}_{2n+2}$), considered as models for polyethylene. Further, it allows the generation of a glassy structure in which molecules are fixed. However, a limit in the simulations quickly appears when the number of atoms reaches 100 or 120 (i.e. $n > 35-40$ for the *n*-alkanes series). Starting from an isolated chain, a realistic representation of the material must take into account, including (as well as the idealized structural aspects) a certain number of defects. A first category of these defects is formed by physical defects, in which we find conformational disorder (which is the rule in the case of an amorphous structure), the free volume or the presence of voids. The second category

refers to the defects of a chemical nature: inter-chain bonding, chain terminations, chemical irregularities, additives and residues, for example.

In the next section, we recall how the representation in terms of energy diagrams, stemming from inorganic semiconductor physics, can be extended to the case of polymer insulators. This is a necessary step, as molecular modeling calls on band gap concepts, extended energy states compared to localized states, etc. Subsequently, we present a state-of-the-art in this domain referring to recently published works.

3.2.1. *Energy diagram: from the n-alkanes to polyethylene*

Even the very concept of an energy diagram is not totally agreed in the domain of polymers, insulators in particular. Criticisms have been expressed, regarding the very applicability of this concept to insulating polymers, or its usefulness to understand the electrical insulation properties of these media, even if it is admitted that there are few alternatives. But why this reluctance? First, because the communities have different approaches (organic chemistry on one side, solid state physics on the other, to be very schematic), and hence a certain mutual incomprehension. Second, because polymers are complex media. “Defects” in a material with crystalline structure are generally localized and can be identified through a chemical, physical or energetic representation. In disordered media, defects are no longer the exception, but the rule so that the representation of such complex systems is delicate.

The objective here is not to argue or identify the *pros* and the *cons*, but to briefly recall the history and bring out the input of physical and chemical quantum theories. The results of molecular simulation from the last decade to describe the transport and trapping properties constitute real advancements and rely on the concept of the energy diagram. It is, then, important to demystify solid state theories so as to establish a language base common to chemists, physicists and engineers.

Numerous theoretical studies, at different levels of complexity, have been developed around polyethylene, PE. The interest for this material is double: it presents a simple chemical structure and it is the subject of numerous applications in the world of insulation. In order to understand and interpret the experimental results on the band gap of the polymers derived from classical techniques, such as XPS (X-ray photoelectron spectroscopy) or EELS (electron energy loss spectroscopy), band structure calculations have been carried out. These calculations have been made easier by the small size of the elementary cell of the material under consideration. We direct readers, at this point, to the excellent overview by R. Hoffmann *et al.*

[HOF 91], written from an educational perspective and intended to develop a common language for physicists and chemists.

The band structure construction of PE from a series of related molecules, from methane to n -alkanes, is represented in Figure 3.1. In this series, from methane to PE, the number of orbitals increases with the size of the molecule, which leads to a narrower and narrower separation between the electronic orbitals. The extrapolation of a continuous band is therefore an idealized representation of a high number of very close electronic levels. The molecular orbitals merge with the energy domains covered by the bands, which proves the close relationship (and even the equivalence) between the states of molecular energy and those of the crystal passing from molecules to extended chains for these hydrocarbons.

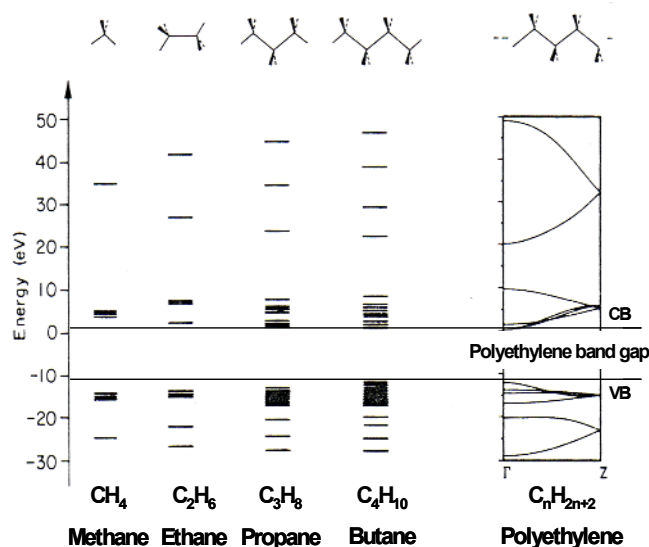


Figure 3.1. Distribution of energy levels of the molecular orbitals from methane to PE in all-trans conformation. The reference for the energies is the vacuum level. The x-axis in the polyethylene band diagram is the wave number (k) scale, spanning from the center ($k=0$, term Γ) to the edge ($k=\pi/a$, term Z) of the Brillouin zone. CB and VB refer to the conduction and valence bands. Adapted from [HOF 91]

From Figure 3.1, we can see that PE is a material with a large band gap, which signifies that there are no energy levels accessible to the carriers between the top of the valence band and the bottom of the conduction band. The width of the forbidden band, whether it is deduced from calculation or experimentally determined, is around 8.8 eV [LES 73], which means that we would have a perfect insulator with an intrinsic conductivity of the order of 10^{-45} S/m [COE 93]. Of course, we know

that such a level of conductivity has never been measured because the reality is far more complex: other levels and processes assist the transport. However, some of these complex features have been studied and form the subject of this section.

Modifications of the “idealized” band structure of PE have been proposed; see for example [DIS 92] as well as the excellent overview by G. Blaise [BLA 01]. Coming back to the fundamentals, two factors must be considered:

– the first is related to the fact that polymer molecules can adopt different conformations, while the linear arrangement, *all-trans*, of lower energy, has been considered until now. These conformations introduce disorder in the organization. Here as well, according to the author’s culture, we talk about physical, conformational or topological disorder. This has consequences for the energy diagram, with the introduction of localized states (accessible to carriers) in the forbidden band. Their density is high (of the order of 10^{22} cm^{-3}) and they are situated in a range of 0.1 to 1 eV with respect to the extended states of the bands (see Figure 3.2). These states are denoted differently according to the author, for example shallow traps, conduction states, or Anderson states. The residence time of the carriers on these sites varies from 10^{-13} s for a level to 0.1 eV to 500 s for 1 eV [MEU 00a,b]. These different terminologies refer to a common physical process: the transport, according to two possible mechanisms. Localized states can be in thermal equilibrium with the extended states of the valence or conduction band, the transport occurring by thermal activation of the carriers toward the bands. This mechanism leads to the transport phenomenon by successive trapping/detrapping, with passage toward the extended band at each step. The term “shallow trap” stems from this approach where the carriers move from one trap to another with a passage by extended levels. The second transport mechanism refers to the possible interaction between localized levels considering their large density (the wave functions of the traps are superimposed). Carriers can then migrate from one trap to another by quantum tunnelling without passing through the extended states defining a tunnel mechanism assisted by phonons (*hopping*). The energy E_c separating extended and localized states is a critical parameter since the mobility of the carriers increases abruptly beyond this value by passing from the effective mobility associated to the transport in the localized states (controlled by the residence time of the carriers in the traps), to the band mobility (free electrons in the conduction band, free holes in the valence band). Some descriptions of the electronic carriers’ behavior under very high electric field consider that the mobility of the carriers is null for energies $< E_c$ and infinite above it, the hypothesis on which is based the field limited space charge model (FLSC) initially proposed by H.R. Zeller [HIB 86], and subsequently refined by S. Boggs [BOG 05];

– the second factor concerns chemical disorder. It can be related to the presence of one or several atoms or bonds non-representative of the monomeric unit, or the

isolated molecules. In PE and in polymers in general, it can be a matter of intra-chain defects (unsaturation, lateral groups, bonding, chain ends), additives (antioxidants, catalysts), reaction residues (cross-linking, for example), and impurities (pollution) which introduce the concept of impurity states [BLA 01]. Chemical disorder introduces physical disorder in turn in its environment, owing to the difference in size and position of the atoms constituting the defect. The electronic properties of the defect are different from that of the host medium, so new energy levels can be introduced in the band gap, generally as deep levels (see Figure 3.2) and with a lower density than the traps known as shallow traps (as we shall see later). It is generally admitted that these energy levels control the space charge phenomenon: we talk about “deep traps” or “real traps” because their contribution to the conduction processes is weak, unlike physical traps which assist transport.

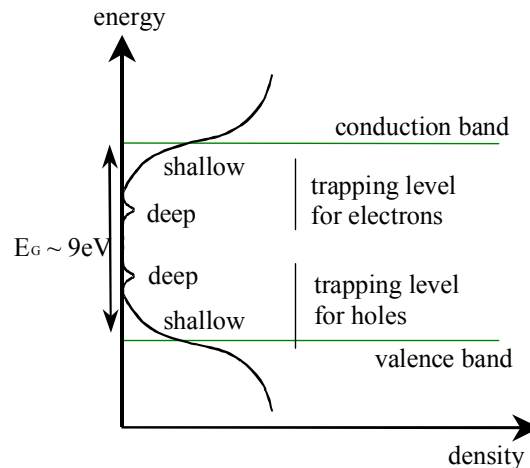


Figure 3.2. Schematic representation of the density of states in a disordered dielectric. The deep and shallow traps are respectively related to the chemical and physical disorder

Having said that, other processes can have a large influence, or even control the electric behavior of insulators: the presence of ions, electrochemical phenomena, for example. From another point of view, the formulation of technical polymers can be so complex that it becomes delicate to distinguish additives from the matrix... All these parameters must be taken into account to determine if the band model that we conceive can adjust to the structure that we process. It is nonetheless true that the band diagram constitutes a fundamental support for the understanding and the development of models.

3.2.2. Results of modeling

3.2.2.1. *N-alkanes models of polyethylene*

We have already seen (Figure 3.1) that the *n*-alkanes series represent a reasonable model of polyethylene with regard to the characteristics of the band gap. Further, the behavior of an excess electron in *n*-alkanes has been thoroughly studied and remains a paradigm for the behavior of excess carriers in dielectrics. Numerous experimental and simulation work has been done on low field mobility, the optical absorption associated to excess electrons or the properties of the forbidden band. They show that the properties of PE become very close to those of the *n*-alkanes with *n* of the order of 15 to 20 at the minimum [PIR 76], even though this assertion is to be adjusted considering recent results showing a difference of 0.2eV in the position of the minimum of the conduction band of PE and C₂₇H₅₆ [CUB 03a,b]. Previous experimental measurements on the hexatriacontane (solid) C₃₆H₇₄ and on other paraffins have been made to extrapolate the electronic and electrical properties of PE [REI 90], [RAC 87], [VAN 62]. Recent molecular simulations have relied on the *n*-alkanes to approach the properties of PE: molecules such as C₉H₂₀ [MEU 97], C₁₃H₂₈ [MEU 98], [MEU 00a,b], C₁₅H₃₂ [MEU 97] and C₂₇H₅₆ [CUB 03a,b], [CUB 02] have been considered.

3.2.2.2. *Volume properties: amorphous and crystalline phases*

Most calculations on the electronic structure of polymers use methods ranging from semi-empirical or *ab initio* approaches to DFT [MIA 96], the latter being less widespread. While the states of valence bands have been well characterized, those of conduction bands, which are, however, of capital importance in transport, have not been so characterized. It is only very recently that studies on the electronic and structural properties of valence and conduction bands have been made. The first report on this subject, concerning purely crystalline PE in its orthorhombic crystallographic form, dates back to 1998 [SER 98].

Using DFT and similar techniques, it was possible to describe the nature of non-occupied electronic states (the conduction band) and occupied states (the valence band). It was then shown that conduction states have an interchain character (the wavefunction is maximum at the half-distance between chains, so at about 5 Å from the chains) while the valence band states have an intrachain character [SER 00]. In a solid, the electronic affinity (E_A) is the energy required to carry an electron from the vacuum level to the conduction band (see Figure 3.3).

It has long been known that PE has a negative electronic affinity, which signifies that the lowest state of the conduction band is situated above the vacuum level [LES 73], [RIT 82]. The interchain character of the conduction states provides a physical interpretation of this phenomenon. A “free” electron would thus be directed

toward the regions of weaker density, such as the surface of the crystalline lamellae, or to an internal cavity. However, although the crystalline PE and alkane crystals present a similar structure as well as a negative electronic affinity, the conduction processes in both materials are different: it is interchain in PE and interlayer in the alkanes (the alkane molecules are organized in layers, which structure the interlayer zones with a weak density). This defines the limit of similarity between PE and the *n*-alkane series [CUB 03a,b]. Another important conclusion can be drawn concerning the conduction by holes in the valence band. If the holes are confined in the chain while the electrons are excluded from it, a distinction between conduction paths for electrons and holes appears probable [LEW 02]. Furthermore, if we take into account a heterogenous density of PE at the local scale, the electrons, which contribute to the space charge phenomenon, have to be uniformly spread out at a nanometric scale. Other publications by different groups [CUB 03a,b], [CUB 02] confirm the interchain character of the wavefunction of the excess electrons in the conduction band.

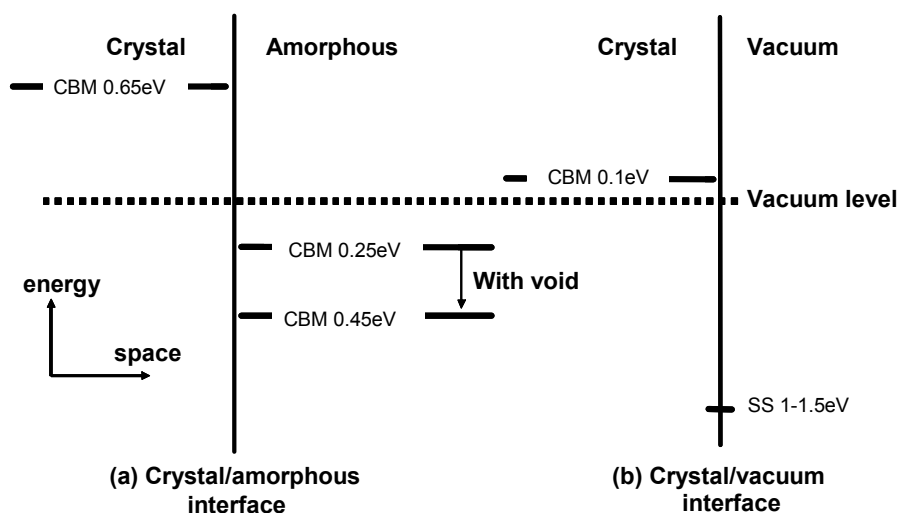


Figure 3.3. Schematic representation of the position of the conduction band minimum (CBM) with respect to the vacuum level of PE. (a) amorphous-crystal internal interface; (b) crystal-vacuum external interface; E_A is the electronic affinity, defined as the energy difference between CBM and vacuum level. It is negative (by convention) for crystalline PE in volume (-0.65eV) and on surface (-0.1eV), and positive for amorphous PE in volume. A surface state (SS) able to assist the injection is represented. A void in the amorphous phase behaves like a trap. Traps introduced by physical or chemical defects are not represented

A fundamental energy state of 0.65 eV has been identified as the bottom of the conduction band, which brings the electronic affinity of polyethylene to

approximately this value; however, all the factors have not been taken into account. At a temperature of 300K, disorder is introduced in the crystalline regions by thermal activation, in the form of a structural parameter distribution (with rotation around the bonds) in respect to their value at 0K. This introduces localized states which can play the role of electron traps (see section 2.1) with depths of the order of 0.1 to 0.2 eV.

The amorphous regions have been modeled by considering a unique chain composed of 360 atoms [CUB 02]. The fundamental energy state (conduction) has been situated at -0.25 eV, i.e. it is localized below the vacuum level, which brings about significant differences between the amorphous and crystalline phase properties. The amorphous regions behave like trapping sites (of a depth of the order of 1 eV) with respect to the crystalline phase. The interfacial regions between amorphous and crystalline phases would also act as traps. For materials with a weak crystallinity rate, the conduction is probably dominated by trapping/detrapping phenomena in the amorphous phase of PE.

3.2.2.3. *Surface and nano-void properties*

The electronic properties of the surface of a PE crystal (at the interface with a vacuum) have been studied considering different orientations of crystals (and so of the molecules) with respect to the surface [RIG 01]. The surface has a negative electronic affinity, like the volume of PE, with energies of -0.17 and -0.10 eV for chains respectively parallel and perpendicular to the surface. The two types of surface have surface states with energies of -1.2 ± 0.5 eV with respect to the conduction band minimum in the volume. This signifies that an electron situated near a cavity in the volume of the PE crystal will be spontaneously emitted in a vacuum (or in a cavity) and the surface represents a deep trapping state with respect to the volume of the crystalline PE. The creation of nano-voids in the amorphous PE brings the fundamental energy state to -0.45eV. The wave function of an electron is then centered on the cavity [CUB 02], which then behaves like a trap.

3.2.2.4. *Trapping sites*

The objectives here are to calculate the energy levels associated with physical or chemical defects in a given environment, in order to determine if these sites constitute potential trapping sites. This principally concerns electron traps, even though some calculations have been made for the holes. The trap depth is defined with respect to the electronic affinity of the system, estimated with and without the defect as illustrated in Figure 3.4. A positive value of E_t represents a potential well for the electron, since in this case the electron has more electronic affinity for the trap than for the material without defect, and similarly for the holes.

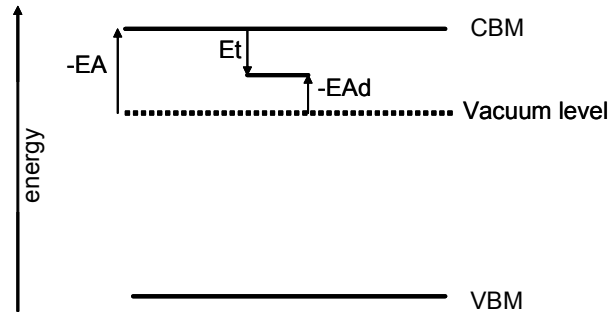


Figure 3.4. Definition of the trap depth for the electrons ($E_t = E_{Ad} - E_A$), where E_{Ad} is the electron affinity of the defect and E_A that of the matrix without defect. VBM and CBM are the minima of the valence and conduction bands

3.2.2.4.1. Physical defects

The first calculations [MEU 97], [MEU 98] were made based on tridecane ($C_{13}H_{28}$) in its minimum energy configuration (*all-trans*), thus giving the reference for electronic affinity. The conformational disorder of PE has been simulated from the crystalline phase of the tridecane by molecular dynamics. The conformational defects thus produce shallow traps (<0.3 eV) [MEU 00a,b], with density of the order of 10^{+20} cm^{-3} , for an average intertrap distance of 15 \AA . The residence time in the traps is of the order of 10^{-11} to 10^{-13} s, which appears consistent with the fact that these sites assist the transport but do not permit the stabilization of the charges which we detect in the long term by classical techniques (hence the term “localized conduction states” rather than “traps”). This first approach was limited to the effect of conformational defects with respect to an *all-trans* structure and did not take into account the density fluctuations of the amorphous phase nor the energy states for excess electrons in the crystalline phase of PE.

A finer approach of the amorphous phase properties has subsequently been developed, relying on the pseudo-potential technique [CUB 03a,b]. The electronic states and the mobility of excess carriers have been deduced for the amorphous PE. The minimal energy states have thus been situated below the vacuum level, at $E_c = -0.32$ eV (compared with -0.25 eV in Figure 3.3) and the mobility limit (E_o) is very close to the vacuum level, which leads to trap depths related to local disorder of the order of 0.3eV (very close to previous estimations). This results in an expression for the mobility of the form:

$$\mu = \mu_o \cdot \exp\left(-\frac{E_c - E_o}{kT}\right) \quad [3.1]$$

where μ_o has been estimated at $7.5 \times 10^{-2} \text{ m}^2/\text{V.s}$, giving a mobility of $2 \times 10^{-7} \text{ m}^2/\text{V.s}$ with an error bar of a factor of 10. Equation [3.1] is valid in the limit $E_o - E_c \gg kT$ and comes from an approximation of the Kubo–Greenwood relation [CUB 03a,b].

3.2.2.4.2. Chemical defects

Two groups of chemical defects have been considered with $\text{C}_{13}\text{H}_{28}$ as a reference molecule in *all-trans* conformation for the electronic affinity. The first group concerns chain imperfections (hydroxyl and ketone functions, double or triple bonding, branching, etc.) and has been simulated by bringing a chemical defect on to the alkane chain [MEU 00a,b], [MEU 01]. The modification of the minimal energy of conformation due to the integration of the defect has been taken into account here. We can see in Table 3.1 that the defects containing carbonyl groups or double bonds form the deepest electron traps. The second group concerns crosslinking by-products of PE [MEU 97]. Among those, acetophenone and α -methylstyrene have been identified as deep electrons traps. The affinity of the holes has also been considered for some of the species in order to estimate their propensity to stabilize positive charges [TEY 01a,b]. A summary of trap depths thus estimated is proposed in Table 3.1, where most values have been deduced without taking into account the polarization that the neighboring molecules can generate on the model chain.

To estimate this polarization effect, calculations have been made on a *cluster* model where the defect is surrounded by alkane chains [MEU 01]. The modifications made have been minimal in this case. However, polarization effects can be significant in the general case, in particular for polar polymers [EKS 68]. Finally, the trap depth of chemicals present in the semi-conducting screens of cables, and likely to diffuse in a PE insulator, have recently been published [CAM 02].

3.2.2.5. Self-trapping and polaron concept

The molecular modeling presented so far has neglected the local changes of conformation associated with the presence of trapped charges. Now, it has long been known that an excess charge in a dielectric polarizes the medium [BLA 01], [BLA 98], see Chapter 2, section 2.3.

In practice, an electron with kinetic energy greater than 10 eV can be considered as mobile in a medium with vacuum permittivity, i.e. there is no perturbation of molecules due to the displacement of these charges. Conversely, a “thermal” electron moves in a polarized medium, whose permittivity $\epsilon(\omega)$ varies radially around the charge starting from the vacuum permittivity near the charge to the static permittivity $\epsilon(0)$ at long distance [BAI 89], [TAY 92]. The radial variation of the polarization around the charge can be taken into account by introducing a polarization charge density, which leads to the *polaron* concept originally introduced by Landau [FRÖ 63].

This phenomenon leads to the gradual confinement of the charge in a potential well whose depth increases when kinetic energy is reduced. This has direct consequences on the energy stored in a material in the presence of a space charge, and on transport. The polarization energy due to a trapped charge can be of the order of 1 to 10 eV for usual inorganic insulators, depending on their dielectric susceptibility [BLA 98]. A polaron formed by capture of an electron by a shallow trap will behave like a particle with high effective mass, the charge “transporting” its own polarization field.

Nature of the defect	Molecule with:	Trap depth (eV)		
		electrons	holes	
6-tridecene* (C ₁₃ H ₂₆)	In-chain C=C	0.16	0.57	
5,7 tridecene* (C ₁₃ H ₂₄)	In-chain conjugated C=C	0.51	1.35	
6-tridecanone* (C ₁₃ H ₂₆ O)	Side chain C=O	0.49	0.43	
5-decanone** (C ₁₀ H ₂₀ O)	Side chain C=O	0.453		
5-decene** (C ₁₀ H ₂₀)	In-chain non-conjugated C=C	0.122		
4, 6-decene** (C ₁₀ H ₁₈)	In-chain conjugated C=C	0.443		
5-decyne** (C ₁₀ H ₁₈)	In-chain non-conjugated C≡C	0.041		
5-vinyl nonane** (C ₁₀ H ₂₀)	Non-conjugated C=C	0.157		
5-decanol** (C ₁₀ H ₂₁ O)	Hydroxyl	0.186		
5-decanal** (C ₁₀ H ₂₀ O)	Carbonyl group	0.445		
4-propyl heptane** (C ₁₀ H ₂₂)	Saturated	0.121		
Crosslinking by-products with dicumylperoxide as crosslinking agent	α -methylstyrene* (C ₉ H ₁₀)	Aromatic	1.53	0.79
	Cumyl alcohol * (C ₉ H ₁₂ O)	Aromatic + Hydroxyl group	0.28	0.36
	Acetophenone* (C ₈ H ₈ O)	Aromatic + Carbonyl group	0.9	0.04
	Cumene** (C ₉ H ₁₂)	Aromatic	0.04	

Table 3.1. A summary of trap depth values estimated by ab initio methods for chemical traps of PE. *from [TEY 01a,b], **from [MEU 01]

Let us consider now how this effect has been evaluated in organic materials. Some modifications of the trap depth by molecular reorganization have been brought to the fore in fluid alkanes [SHI 72], [WIL 73], [ABR 92]. The stabilization of excess electrons in the hydrocarbons has been particularly studied by means of optical absorption spectroscopy. The stabilized electrons form absorption bands in the near infra-red, which move toward the shorter wavelength over time, this being clearer in polar matrices than in hydrocarbons. This phenomenon has been attributed to a strengthening of the trap by reorientation of the surrounding molecules [KLA 72]. Experimental evidence of a trap deepening by rotation of the molecular dipoles has been reported on the basis of recombination-induced luminescence

experiments on a model molecule frozen in a glass [HO 77]. In solid polymers, the polarization energy will lower the energy state of an electronic trap (in reference to the vacuum level) [LEW 02]. For certain polymers, notably those composed of lateral groups, the energies at work can be of 3 eV [DUK 78]. As for PE, the calculations made so far neglect the molecular reorientation associated with the excess electrons. If the approximation is acceptable for treating extended states (the environment not being very perturbed by the moving electrons), this becomes more debatable for trapping sites. Preliminary calculations taking into account these effects in the case of extended states show that, after a certain time, the electron “traps itself” with an energy corresponding to the bottom of the conduction band. The variation of energy at work is weak here (0.1eV, being in the error bar of the simulation method), as expected for a non-polar material [CUB 03a,b]. For a chemical trap, the problem has not been treated but should be, in particular for polar polymers where the polarization energy can be very significant.

3.3. Macroscopic models

The layman might wonder why the models for describing transport in polymer insulators are so numerous and so disparate in their hypotheses, whereas transport, Poisson and continuity equations are very general since they are valid for semi-conductors, dielectrics, but also for solid, liquid and gaseous states. A first answer can be found in the fact that, in electrical engineering, the research strategies, from where scientific developments ensue, are led more by system-oriented rather than materials-oriented approaches. Further, for organic semi-conductors, the experimental behavior is generally more satisfactorily described by available physical models than for insulators. To dwell on this comparison, a certain number of specificities of polymer insulators need to be underlined:

- the complexity of the very structure of the materials. Polymers have a complex physical structure (amorphous and crystalline regions, chain conformation, etc.) and chemical structure (branching, in-chain defects, residues, additives, etc.). These issues have been broached in the previous section;

- response time. Transient phenomena in semi-conductors are fast, such that, quite often, the physical models are only solved in stationary conditions [WAL 02], [TOR 84], [SHE 98] by taking into consideration processes such as injection, transport and recombination. Conversely, transient responses in the insulators are very slow, such that we never know if a stationary regime is reached. This is why the models are defined and established in a way that respects the time scale of these devices. For years, studies on transient phenomena in insulators have been made by macroscopic observations, such as charge or discharge currents or surface potential measurements. The more recent measurements of internal charge densities have had a considerable impact on the evolution of models dedicated to simulation, by

considering new processes to insert in analytical and/or numerical modeling. Another problem concerning the behavior of insulators is the superimposing of two physical phenomena: polarization and space charge [WIN 88], [SHO 71]. The very representation of the dipolar response of polymers is debated, with diverse approaches ranging from the “universal” relaxation law [JON 96] to mode-coupling theory [RAJ 91], and to distributed processes [BOT 78]. The minimum we need here is to have a good approximation (by independent measurements and phenomenological simulations) of the response in polarization alone. However, it is not obvious to obtain this kind of information when the polar species are molecules in weak concentration, like in PE and in materials which are not generally very polar;

– the variety of phenomena potentially involved in transport. This concerns the hypotheses taken concerning the origin and nature of carriers and traps, as well as the transport and trapping mechanisms. While the previous models for describing the transient currents and voltage/current characteristics are based on a unique species of carriers, the space charge measurements show that transport is, most often, bipolar. In the same manner, it is not conceivable to imagine a generation of charges only by intrinsic processes, since the space charge measurements show the accumulation of homo-charges near the electrodes.

Next, we consider the different physical phenomena which have been inserted in the macroscopic models. The problems related to the choice of numerical methods, algorithms and meshing [WIN 03a], [WIN 03b], will not be discussed here. Whichever physical model of transport is considered, and neglecting the polarization, the mathematical problem is reduced to equations [3.2], [3.3] and [3.4] below, considering a 1D problem along the spatial coordinate x .

$$j(x,t) = \mu E(x,t) \cdot \rho(x,t) - D \frac{\partial \rho(x,t)}{\partial x} \quad [3.2]$$

$$\frac{\partial \rho(x,t)}{\partial t} + \frac{\partial j(x,t)}{\partial x} - D \frac{\partial^2 \rho(x,t)}{\partial x^2} = s(x,t) \quad [3.3]$$

$$\frac{\partial E(x,t)}{\partial x} = \frac{\rho(x,t)}{\epsilon} \quad [3.4]$$

where j is the current density for each type of species, e the elementary charge, μ is the mobility, D is the diffusion coefficient, E is the applied field, ρ is the net charge density. Equations [3.2] and [3.3] must be written for each type of carrier defined in the model. The term s is the source term which represents the local density changes due to processes other than the transport, such as the internal generation, the recombination, etc. These equations can have a specific form for the interfaces and are completed by the different boundary conditions like applied voltage.

Whatever the system considered, there are at least two processes to define the construction of the transport model: how the carriers are generated and how they are transported. Most often, the models are defined for two types of charged species (which are not necessarily mobile) and therefore an additional set of physical phenomena must be considered defining the interactions or exchanges between carriers of different types. In the sections below, a description of these two processes (generation and charge transport) is first made. Then, an analysis is made of how these elementary mechanisms have been combined to supply a set of results which enable the experimental behavior of insulating polymers under electrical stress to be approached.

3.3.1. *Elementary processes*

3.3.1.1. *Generation of charges*

If we set aside the generation of charges due to discharges in the insulation environment, and all other sources of irradiation (photo-generation, X-rays, electronic irradiation, etc.), several mechanisms still remain for the generation of carriers, namely: electrode injection, ionic species and donor states.

3.3.1.1.1. Electrode injection

The most discussed mechanism to describe charge injection in organic semiconductors is the Schottky effect, also known as field assisted thermo-ionic emission [DIS 92], [DWY 73] where the dependence of the current density, with field, is in the form of $\exp(E^{1/2})$. This law is also used in insulators, with (however) some inconsistencies on the parameter values: the experimental value of the injection barrier (around 1 eV) is much smaller than the presumed value for a dielectric-metal contact (about 4 eV, depending on the material). Furthermore, the pre-exponential factor is much smaller than expected [DIS 92], [HUG 80]. One of the reasons for such a low injection barrier could be that the conditions for which the work functions have been measured (clean surfaces in the ultra vacuum) are no longer respected when we work in normal conditions: the interfaces must present far more imperfections. Another injection process currently touched on is injection by field effect, also known as the Fowler–Nordheim effect [DWY 73], generally when the electric field is very high (beyond 100 kV/mm).

Apart from these two models, we find some alternative descriptions for charge injection, notably by thermally assisted quantum tunneling from metal to localized states [ABK 95], quantum tunneling toward polaron levels in the polymers [CON 97], injection limited by interfacial states induced by the dipoles [BAL 01], thermally-assisted injection in a random *hopping* system, [ARK 98], Schottky emission limited by diffusion [EMT 66], [SCO 99], or hot carrier injection followed

by a thermalization and a carrier motion, according to the Onsager theory [BLO 74]. Further, a certain number of models suppose a constant charge density or an infinite reservoir of charges on the electrodes (ohmic contact). The current is then entirely controlled by the volume transport.

3.3.1.1.2. Internal generation

A weak concentration of ions can be present in polymer materials, associated for example with chemical reactions implying sulphur present in the antioxidants or organic ions resulting from the oxidation of the polymer [GIL 92]. An alternative to ion generation is the dissociation of impurities or water molecules under the influence of an electric field – referred to as the Onsager mechanism [PAI 75]. Finally, ionic species can be generated at the metallic or semi-conductor electrode level and diffused within the dielectric [TAK 99a,b], [HO 01]. As an example of transient current simulation, let us cite Kahn and Maycock [KAH 67] who have considered a bipolar ionic model with blocking electrodes. The transport is controlled by diffusion and effective mobilities are also defined. Iwamoto [IWA 96] has considered other mechanisms, a *hopping* conduction and blocking electrodes in the case of ionic impurities blocked at the interfaces.

Carriers in the volume (for example, the electrons) can originate from donor states, and the hole thus generated could be mobile or not. Extraction from donor states can be produced from processes such as the Poole–Frenkel effect [RAS 02].

3.3.1.1.3. Carrier extraction

According to their nature, the carriers can be extracted or not by the opposite electrodes. In the case of ions, it is difficult to envisage mass transport through electrodes. This is why ions can be considered blocked at the interfaces [IWA 96]. However, they can interact with carriers with opposite polarity injected at the electrode, thus re-establishing electrical neutrality. In the case of electronic carriers, extraction can be made with or without an extraction barrier.

3.3.1.2. Charge transport

The charge transport processes first depends on the nature of the carriers. The first classification is a distinction between ionic and electronic processes. In electronic processes, a second classification can be established depending on whether the transport is made via the conduction band (Poole–Frenkel mechanism) or not (*hopping*). The Space Charge-Limited Current (SCLC) descriptions are based at the same time on an “ohmic” type of conduction (with a band mobility or limited by traps) and on a distortion of the local electric field due to the accumulation of space charges. This is why this model is not considered as an elementary mechanism. Figure 3.5 shows some basic mechanisms concerning electronic transport.

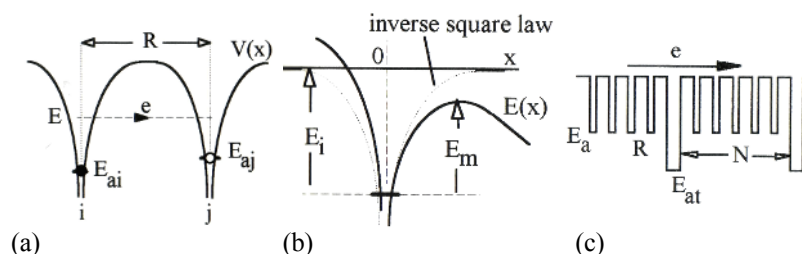


Figure 3.5. Some basic mechanisms of the transport [LEW 98]. (a) Tunnel resonating between two states. Here, i and j are acceptor states. (b) Poole-Frenkel. (c) Transport controlled by traps: the mobility depends on the average residence time of the carriers in the traps

3.3.1.2.1. Hopping conduction

The process by which an electron can move from one place to another is made by thermal excitation above a potential barrier, by quantum tunneling through the barrier, or by a combination of both phenomena. The *hopping* conduction corresponds to an intermediate situation in which an electron is brought by thermal activation to a level of similar energy to that of an empty site towards which it moves by quantum tunneling [DIS 92]. The hopping probability depends on the field. In a more general manner, the term refers to the mechanisms which do not involve the conduction band (or the valence band for holes).

In applications such as photocopiers, where charges are generated in a similar manner to time-of-flight type experiments, the transit of a charge occurs with a time-dependent mobility. This phenomenon, called *dispersive transport*, has been interpreted by a hopping frequency distribution, associated with an inter-site distance. It has been described in the frame of random walk theory [SCH 75]. The models based on this approach have attempted to explain the Poole-Frenkel law for mobility [EKS 68], [DUN 95] – see the bottom two rows of Table 3.2.

3.3.1.2.2. Poole-Frenkel Effect

The Poole-Frenkel mechanism in the volume is analogous to the Schottky injection at the metal-insulator interface. This mechanism is based on the decrease of the potential barrier height needed to get over by application of an electric field. It applies to deep donor (or acceptor) states in insulators with a large gap. This process is subject to strong controversies [WIN 99], [PAI 75], [WIN 98]. Indeed, the barrier maximum is at a further distance from the site than the diffusion length, such that the excited electron has a high probability to be thermalized before it gets over the barrier. The observed slope on the curve $j(E^2)$ is often smaller than expected, and the observed low field saturation is not explained. Finally, another problem is the lack of evidence for the presence of donor states in the polymers, even though this

hypothesis can be found in recent models. An alternative process, judged more “physical” and based on the Onsager dissociation theory, has often been proposed as an alternative to the Poole–Frenkel mechanism [BLO 74], [PAI 75].

3.3.1.2.3. SCLC models

The main objective of models based on the Space Charge-Limited Current (SCLC) is to determine the external current under steady state regime in conditions where the carrier concentration is sufficiently high to produce a significant variation of the electric field and, therefore, a variation in the carriers drift velocity. These models enable the external current of electronic carriers to be estimated, in a medium without traps, with only one level of trapping, or with an exponential distribution of trapping levels [ROS 55], [MAR 62]. In the simplest version, the free carriers have a band mobility and the contacts are assumed to be ohmic. Besides, the non-linear character of the current/voltage characteristics under a stationary regime has led to resolutions in a non-stationary regime [MAN 62], [ZAH 74], [HAR 75]. Finally, improvements have been made by taking bipolar models, mobility functions of the electric field and the distributions of traps into consideration [LAM 70], [NAT 02].

3.3.1.2.4. Ionic conduction

The carriers are considered thermally activated above a potential well. When a field is applied, the potential barrier in the direction of this field decreases (and increases for the opposite direction), thus increasing the probability that the carrier will be directed in the direction of the field. A field-dependent mobility derives from this simple outline, the first reference to a *hopping* type mobility (a variation of $sh(E)$) for ions dating from 1948 [MOT 64].

3.3.1.2.5. Diffusion

Diffusion is a natural motion of species – atoms, molecules, ions [MUL 94] or electronic carriers [TOR 84] – which is due to a gradient of chemical potential. At a first approximation [MUL 94], transport by diffusion can be seen as the first derivative of species concentration in the three directions of space, see equation [3.2]. For a highly diluted ion solution, mobility is related to the diffusion coefficient by the Nernst–Einstein equation:

$$\mu = \frac{qD}{kT} \quad [3.5]$$

This relationship supposes that ion mobility is closely related to the molecular motion within the polymer [BAM 03]. In polymers, diffusion is often neglected in

the transport equations. This does not signify that the elementary transport mechanism is different, but that equation [3.2] can be approximated by solely considering the drift current:

$$j = \mu e \left(E n - \frac{kT}{e} \frac{\partial n}{\partial x} \right) \cong \mu e E n \quad [3.6]$$

The hypothesis of negligible diffusion comes from the fact that the concentration gradients are generally not very significant, but also that the nature of ions is uncertain and therefore identical for the coefficient values. Indeed, even when the simplest case of neutral species is considered, the diffusion coefficients can change in a very significant manner, according to the size of the molecules which diffuse. In the case of ions, other phenomena add up, such as the electrostatic and polarization interactions with the matrix and inter-ion interactions [MUL 94].

3.3.1.2.6. Mobility

With regard to electronic transport in disorderly materials, the mechanism generally admitted for the transport is *hopping* conduction [DYR 88], implying a diagonal disorder (see Figure 3.5), or off-diagonal; see [BAS 93] for a detailed description. Thus, mobility would be more related to one or the other of the elementary mechanisms described above than to conduction in the extended states. This is why, for each of these mechanisms (SCLC, *hopping*, Poole–Frenkel, etc.), the dependence in field and temperature of the mobility is either explicitly defined, or described by hypothesis; see Table 3.2. We should point out here that we do not refer to ohmic conduction as a basic mechanism for charge transport; here, it can be a band mobility, improbable in polymeric insulators, or a trap limited ohmic conductivity. In the case of shallow traps where the charges, near the conduction band, are in thermal equilibrium, the apparent mobility is weaker than band mobility, in a ratio corresponding to the ratio between the time spent by the carriers in these traps and the time spent in the conduction band [DIS 92]. The resulting expression is a mobility independent to the electric field. This model is commonly used to describe charge transport.

So far, only one energy level has been considered. When the trap depths are distributed, the situation becomes much more complex. Indeed, interactions between the different trap levels must be considered. In the same manner, a distribution of inter-trap distances can considerably change the results from a numerical simulation. Such a disorder is expected in polymer materials, but supplying a detailed description of these traps (in terms of depths, distances, etc.) is a much more difficult problem.

Process	Expression for the effective mobility	References
ionic conductivity: low field	$\mu = \frac{\alpha}{kT} \exp\left(\frac{-\beta}{kT}\right)$	[DWY 73]
high field	$\mu = \frac{\alpha}{E} \exp\left(\frac{-\beta}{kT}\right) \text{sh}\left(\frac{\gamma E}{kT}\right)$	[DWY 73]
SCLC – space charge limited current	$\mu = \alpha \exp\left(\frac{-\beta}{kT}\right)$	[DIS 92]
<i>Hopping</i> : above a potential barrier	$\mu = \frac{\alpha}{E} \exp\left(\frac{-\beta}{kT}\right) \text{sh}\left(\frac{\gamma E}{kT}\right)$	[MOT 64]
through the barrier	$\mu \propto \exp\left(\frac{-2\alpha}{3kT}\right)^2 \exp\left(\frac{\beta\sqrt{E}}{(kT)^2}\right) \exp(-\gamma\sqrt{E})$	[WIN 03]
Poole–Frenkel	$\mu = \alpha \exp\left(\frac{-\beta}{kT}\right) \exp\left(\frac{\gamma E^{1/2}}{kT}\right)$	[JON 67]

Table 3.2. Some expressions for mobility as a function of electric field and temperature. α , β and γ are constants

3.3.2. Some models characterizing the experimental behavior

In the literature, most of the articles dedicated to the modeling of charge transport are models established to recover current/voltage characteristics under a stationary regime. Only a few articles allow estimates of the external current under a non-stationary regime: they are subject to the first part of this section. Among these articles, only a few models are capable of reproducing both the external current and the space charge distribution as a function of time. In the second part of the section, a synthesis of these different models is proposed. For each model, a detailed presentation of the hypotheses, considered physical phenomena and results obtained is given. Finally, we consider high field models, whose principal difficulty consists of simulating charge packet phenomena.

3.3.2.1. Transient current models

Most of the models were established in the 1970s, to address problems related to semi-conductors and insulators used in reprography systems [SCH 75], [HAR 75], [LAM 70]. Transient currents have been simulated within the framework of the SCLC model [MAN 62], [MOR 62], [HEL 62]. In the Many and Rakavy model [MAN 62], a single carrier type was considered and only one trapping level is defined. The contacts are assumed to be ohmic.

Figure 3.6 shows the shape of the transient current. When there is no trap (a) or when the traps are shallow (b), a current peak is observed at the moment when the principal charge front reaches the opposite electrode. When the traps are shallow (c),

the trapped charges accumulate near the electrode where the carriers are injected; this phenomenon induces a decrease, then a vanishing of the current density. It is obvious that this decrease will be even faster, as the trapping probability will be high. Iwamoto [IWA 96] has simulated transient currents produced by ion transport with extraction blocking. Only one carrier type is considered, with a *hopping* type of transport and including diffusion. The electric field distortions induced by the space charge are integrated. The general form of the current (see Figure 3.6d), is composed of a slight short-term reduction, followed by an increase up to a maximum, and finally a monotonic decrease. Despite being completely different hypotheses, these two models give similar results: the curves obtained look practically the same.

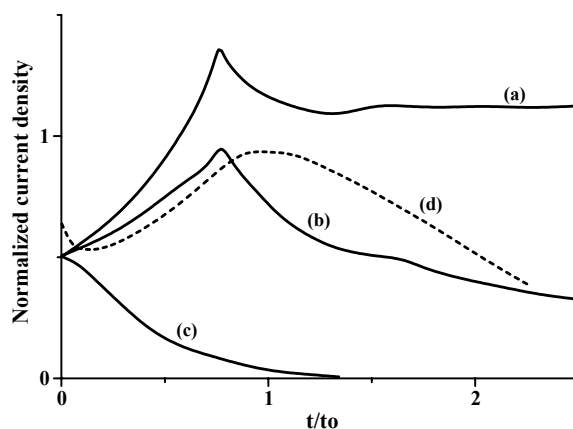


Figure 3.6. (a–c): Transient current in a space charge limited model for a step-like applied voltage (a) no trapping; (b) moderate trapping; (c) strong trapping. t_0 is the carriers transit time in the absence of space charge effect. Adapted from [MAN 62]. (d): transient current for an ionic transport and blocking electrodes. The time is in arbitrary units. Adapted from [IWA 96]

3.3.2.2. Models associated with the space charge measurements

The physical processes which potentially contribute to the transport and generation of charges, presented at the beginning of this section, and the complexity of the materials studied show the difficulty, for modelers, of identifying simplifying hypotheses. Until now, experiments and simulations, permitting the dynamics of space charges in the organic insulators to be characterized, have been combined only for polyethylene-type materials. The different data obtained by space charge measurements on these materials indicate the necessity of considering the deep trapping notion at the same time for positive and negative charges [TEY 01a,b], [ALI 94]. In the same manner, the recombination of charges must be considered to explain electroluminescence phenomena [TEY 01a,b]. Hence, there are a number of

observations, going from space charge profiles, to conduction current and to electroluminescence measurements, which force us to consider injection, bipolar charging processes, deep trapping and recombination phenomena. The goal is to establish models capable of explaining a maximum of experimentally observed physical phenomena, which inevitably leads to a parameter vector to adjust, generally of high dimension, in a way such as to approach experimental measurements [WIN 03]. The obtaining of a set of parameters giving acceptable results (by comparison with the experiment) does not necessarily signify that the physical processes inserted in the model are exact. The solution, to reinforce the physical aspects of the established model, is probably to confront results from the numerical simulation with experimental data obtained by using different measurement parameters, different protocols and a large variation interval in temperature, electric field, etc. Unfortunately, the optimization of parameters becomes even more delicate.

The common difficulty to all approaches is how to take into consideration all phenomena related to trapping whilst dismissing those related to conduction. In other words, all of the phenomena must be considered and pondered according to their energy level. As we have already specified, the most commonly used mechanism to describe charge transport in polymer insulators is to define a trap-controlled mobility. The carriers move in the conduction band, for the electrons, (or in the valence band, for holes) and can be trapped in shallow traps by remaining in thermal equilibrium. However, this approach can hardly explain the persistent charge in depolarization. For that, a deep trapping level is introduced. The principal conduction models in the polymer insulators are presented in Table 3.3. All of these models consider bipolar transport and, for some of them, the trapping and recombination phenomena are taken into consideration.

Alison and Hill [ALI 94] have proposed a bipolar model in which the available charge density for the injection is the difference between a constant source density and the trapped charge density near the electrode. Internal generation and diffusion are neglected. The model is intended to describe the behavior of cross-linked PE. Charge transport is modeled using an effective mobility. The trapping for electrons and holes occurs on only one level, without detrapping. Recombination is defined by coefficients, for each combination of species. The results from these simulations are essentially space charge profiles as a function of time. They have been favorably compared to space charge measurements obtained by Li and Takada [LI 92].

Fukuma *et al.* [FUK 94] have developed a more complete model than that previously set out. The generation of charges is made by two-electrode Schottky injection. They also considered the presence of charges in the dielectric before application of a voltage. The transport is described by *hopping*, the two mobile species being able to be trapped for a short time on only one shallow trapping level.

A potential barrier is defined at both interfaces for the extraction of carriers. The recombination between the mobile carriers is taken into consideration. All the barriers (*hopping*, injection, extraction) are symmetrical for both species. As for the previous model, the results are space charge profiles which are compared to the experimental data of Li and Takada [LI 91]. The model has been applied for a material containing an internal interface between two layers of cross-linked PE [FUK 95].

Kaneko *et al.* [KAN 99] have presented a macroscopic model, whose hypotheses are similar to those of Alison and Hill's, the simulated material being low density PE. Bipolar charges are generated by a Schottky type mechanism and the transport is achieved through *hopping*. The recombination between the holes and the electrons is taken into account; there is no deep trapping and the extraction barrier is assumed to be null (by continuous extraction). The results, which are compared to experimental measurements, are space charge and current density profiles. The hypotheses did not permit them to obtain results consistent with experimental data, underlining the necessity to take into account deep trapping effects.

Le Roy *et al.* [LER 04], [LER 05] have recently proposed a model to characterize charge transport, trapping and recombination phenomena, experimentally observed by charge and discharge current measurements, space charge and electroluminescence measurements, for low density PE. The current and charge measurements on "intrinsic" PE (without additives) indicate that electronic processes are dominant [KAN 99], [LER 04], the charges most likely being generated by injection at the electrodes. Furthermore, the space charge measurements do not show any accumulation of hetero-charges during the polarization time, so no extraction barrier has been applied. The model follows the other hypotheses put forward by Hill and Alison [ALI 94], but detrapping is introduced. The approach is justified by the existence of two very distinct zones in the trap energy distribution in polyethylene. The first one, very close to the conduction band, is characterized by trap depths which do not exceed 0.3 eV. The second, due to chemical disorder, ranges from 0.5 to 1.5 eV. The model appears able to reproduce the essential features observed under DC stress: the space charge profiles and their dynamics under polarization and depolarization, the charge and discharge currents and electroluminescence [LER 05]. Regarding the electroluminescence data, a relation has been established for the minimum recombination rate that provides a signal above the noise level of the detection system [LER 04].

Finally, a model has been developed by Boufayed *et al.* [BOU 04], [BOU 05] in which an exponential trap distribution truncated by a maximum depth is considered, the material studied being cross-linked PE. The distribution parameters rely on the distribution of the physical and chemical traps estimated by Quirke *et al.* [MAR 02], [ANT 02] by molecular modeling. The discrete distribution of these traps is converted

into a continuous distribution. Transport is made by a *hopping* type mechanism. Quirke *et al.* suppose that these traps are filled from the lower energy level upwards. The recombination is not taken into consideration here. The results from the numerical simulation are not in total agreement with the experiment [BOU 06], which is explained on the one hand by very interdependent processes (transport, trapping, mobility variation), and on the other hand by the very complexity of the material considered.

The main hypotheses of these different models are summarized in Table 3.3.

Reference:	Alison & Hill [ALI 94]	Fukuma <i>et al.</i> [FUK 94]	Kaneko <i>et al.</i> [KAN 99]	LeRoy <i>et al.</i> [LER 04]
Generation of charges	Constant charge source	Schottky Injection	Schottky Injection	Schottky Injection
Extraction of charges	No extraction barrier	Extraction barrier	No extraction barrier	No extraction barrier
Transport	Conduction by free carrier	Conduction by <i>hopping</i>	Conduction by <i>hopping</i>	Conduction by free carrier
Trapping	Single trap level	Single trap level	Two trap levels	Single trap level with detrapping
Recombination	Between free charges and trapped charges	Free charges	Free charges	Between free charges and trapped charges
Others		Joule effect Charges initially presented		Density of initial charges

Table 3.3. Characteristics of the physical models for bipolar transport

3.3.2.3. High field models

So far, the different models presented have been established for relatively weak fields. In the case of polyethylene materials and for applied fields greater than $70 \text{ kV}\cdot\text{mm}^{-1}$, the space charge measurements – by pulsed electro-acoustic technique (PEA) or by laser induced pressure pulse (LIPP) [KAN 99], [HOZ 94], [HOZ 98] – show repetitive charge waves propagating in the bulk of the insulation, usually referred to as charge packets. These charge packets have been observed for dielectrics of 0.1 mm to a few mm of thickness. The observed oscillations in the current density have clearly been associated with the propagation of charge packets [HOZ 94], [ALI 98]. Indeed, studies have shown that these oscillations, which depend on the field and the material under consideration, have an oscillation period similar to that of the charge fronts. Further, the current peak is associated with the disappearance of the charge packet when it reaches the opposite electrode [ALI 98], [SUZ 98], coinciding with the formation of a new charge front. Finally, the oscillations observed in the electroluminescence signal and the current are

synchronous [TEY 01a,b], which signifies that the rate of recombination is maximal at the moment when a charge front disappears and/or the next one forms.

Numerical models have been made to reproduce these phenomena [LI 91], [HOZ 94], [HOZ 98], the constraints on the predictions being that: (i) charge fronts must form; (ii) they must move; (iii) they must maintain their form during the transit; (iv) the process must be repetitive. Usually, these charge packets appear near an electrode, such that a massive charge injection or an ionization induced by the field have been proposed as mechanism initiators of the packets. A necessary hypothesis for these models is the presence of charges of both polarities, which is in agreement with the observed electroluminescence in these field regimes (associated with the radiative (i.e. giving rise to luminescence) recombination of charges).

Generally, the models consider a two-electrode injection. The principal difficulties encountered in simulation are the attenuation and dispersal of the charge fronts during their transit, and the lack of repetitivity of the phenomenon. The attenuation of the fronts leads to a displacement of a short distance and a limited number of successive fronts. In fact, the form of the charge packet is maintained during the transit only if charges are generated in the volume (as opposed to injection at the electrodes) during the front transit. This generation has been simulated by considering donor centers, or by ionization in the region where the local field is maximal, generally before the charge front [HOZ 98], [FOT 00]. The apparent charge motion would then result from the difference in mobility of positive and negative carriers.

3.4. Trends and perspectives

3.4.1. *Unification of atomistic and macroscopic approaches*

A first step towards a unification of macroscopic and microscopic approaches has been attempted by Quirke *et al.* [MAR 02], [ANT 02] where a prediction of the current-field characteristics of PE has been proposed relying on *ab initio* calculations. The method has three steps:

1. Estimation of energies, density and residence time of the conformational traps of PE, using DFT. A similar approach has been made for chemical traps.
2. Calculation of local electronic mobilities for a transport model by multiple hops including the influence of the traps filling. An important result here is that, even though the chemical traps are largely a minority, electronic mobilities are controlled by the deep traps for low carrier densities.

3. Switch to the macroscopic scale by resolution of the Poisson's and transport equations. The boundary conditions are a constant electrode charge source.

In its current form, the model is limited, in the sense that the transport is supposed to be unipolar (electrons only), where the behavior at the interfaces is simplified and where the agreement with the experimental behavior is approximate, particularly at high field. However, the model is unified in the sense that it gets to a macroscopic description of the transport, starting from the traps' characteristics simply deduced from the physical and chemical structure of the material. To our knowledge, it is the one and only attempt at an integrated model in the insulating polymers domain.

What are the difficulties of using this method? Certainly, the atomistic models are very greedy in terms of computational power. However, progress in this domain has been made, and it does not seem that calculation times are always a limiting factor; in any case they will not remain so. Elementary simulations still suffer from an incomplete description of what these materials really are. Even for the simplest of them (PE), the chemical structure is complex: not all chemical defects are identified and quantified, and the antioxidant chemistry is particularly disconcerting. Certainly, a concentration which is extremely weak in defects or impurities is sufficient to explain the net space charge densities which are measured: by considering the order of 1 C/m^3 for these latter, a charged center density of $6 \times 10^{12} \text{ cm}^{-3}$ is obtained. The repetitive unit density of PE ($-\text{C}_2\text{H}_4-$) being $6 \times 10^{22} \text{ cm}^{-3}$, a density of (charged) defects of 1 in 10^{10} repetitive units is sufficient to explain what is measured [TEY 02]. Such a concentration is beyond the scope of chemical analysis techniques for these materials. It is also immensely weaker than the concentration in any known residue. Thus, occupation of a tiny fraction of potential chemical traps described above is sufficient to describe the experimental behavior, unless the measurement only represents a slight imbalance between positive and negative trapped charges. The same problem is expected for transport sites considering the very high density of estimated physical traps.

The way to establish the continuity between microscopic and macroscopic descriptions is probably to bring quantum calculations to simple (or simplified) outputs, as is the case in the approaches of Quirke *et al.* [ANT 02]. In this example, energy distributions of traps have been produced, indeed by considering a limited number of defects. This type of information can be taken as the starting point of macroscopic models. We expect new developments of these *ab initio* methods, for example to obtain information on hole trapping and transport at the same level as what was done for the electrons, to better define the interactions between electronic carriers (charge recombination), to tackle the internal generation phenomena by dissociation assisted by the field, or to evaluate reactivity of charged centers.

Coming back to macroscopic models, one of the difficulties is that the physical models must be relatively complex to reproduce a continually growing set of experimental observations. This necessarily leads to an increasing number of parameters, most of them being hardly accessible by independent experiments. The numerical techniques can henceforth bring solutions to the physical models in reasonable time, as long as we introduce the right parameters. The problem is that the adjustment becomes tedious when the number of parameters increases, especially if it is empirical (see section 3.3.2). The contribution of inverse methods to adjust these parameters becomes urgent.

3.4.2. Interface behavior

The metal/dielectric interfaces processes are very critical in the sense that, in numerous cases, they control the carrier generation. We have previously shown that a limited number of models are available to account for interface effects. What is more, their relevance is questionable. The Schottky mechanism does not work with theoretical barrier heights. Another problem: the barrier maximum is situated at such a long distance from the electrode that an electron has a very strong probability of being thermalized by collisions before getting over the barrier [WIN 98]. Such a mechanism might explain why apparent barrier heights are weaker than expected.

Alternative interface charge transfer principles have been proposed [LEW 02], [WIN 98], but they remain unverifiable. The analysis of macroscopic behavior is clearly not the most relevant way to identify the interface elementary mechanisms because it does not permit the interface effects to be separated from the volume ones, especially when the volume transport processes are not firmly established. Moreover, macroscopic techniques collect and average the information on a certain sample surface (or even volume), like the current injection models do. The point is that we do not have definitive proof that charge generation phenomena are homogenous processes.

We therefore need specific descriptions of the interfaces concerning the property gradient of the insulator near the surface, and the property limits at the metal (or other)/insulation interface. While methods exist to generate carriers in precise regions of the insulator (volume or near the surface) without activating the injection itself (through implantation by electron beam, for example), there are no routine means for looking at what happens when charges cross the interface. Promising results have been obtained, for organic semi-conductors, by near field potentiometry [SIL 96]; the application of such methods to insulators, and more generally of near field imagery techniques, must be envisaged because they could bring determining information about the interfaces. Interfaces are clearly crucial topics: understanding them will lead to strategies to improve the insulators' performances by specific

processes (surface treatment, etc.) [HAY 90]. The interfaces can also be internal interfaces, as is the case of multilayer dielectrics [SUH 96], [BOD 04], or in the world of composite dielectrics with nanometric charges [LEW 04].

3.4.3. Physical models for transport in volume

3.4.3.1. Identification of the nature of carriers

It is still not clear what the nature of carriers is, as pointed out in [WIN 03], and it could remain thus for a long time considering the complexity and diversity of the phenomena coming into play, in generation and as well as in transport: electro-dissociation, electrochemical reactions, generation of electrically active species of low molecular weight, the role of humidity in transport, trapping, influence on a trapped charge, are all supplementary processes to those described in the previous paragraph, and are all to be envisaged. Further, it can be tricky to distinguish between the electronic and ionic carriers: we are used to considering that electronic transport is carried out without mass transfer, which is true, but the transport of protons can also be carried out without significant mass effects. Another aspect is the coupling of carriers and media. In polar media, a charge can move with its own polarization field, thus behaving like a heavy particle having an apparent charge which does not correspond to an electron charge. Even if many questions still remain unanswered, the important point to consider is the vector dominating the transport for a range of experimental conditions. We have available some experimental evidence concerning the electronic processes in insulating polymers under high fields, and some others involving ionic transport under low fields. These questions could be treated by better focusing the experimental conditions around the methods permitting the evaluation of the spatio-temporal distribution of charges [FLE 05], with good spatial and temporal resolutions. This has not necessarily been the case so far, the methods having been applied more to solve practical questions than to study the fundamental transport processes. For example, when the charge measured under DC stress is of the same sign as the polarity of the adjacent electrode, we suppose it corresponds to the injection and we turn towards electronic transport by hopping. However, species of weak molar weight could stabilize the injected charge and give rise to ionic transport in volume. At the other extreme, when charges accumulate at an electrode of opposite polarity, ionic transport is often invoked, but it can also result from the transit of electronic carriers from the opposite electrode.

3.4.3.2. Trap identification

The nature of traps are always debated, and we have argued chiefly according to the philosophy stemming from semi-conductor physics and dielectrics theory, in which the polaron is relevant. A set of techniques have been implemented to identify

the nature of traps, but they do not necessarily appear consistent [WIN 90], [WIN 03]. There is still no consensus on the interpretation of measurements in terms of localized states formed by the polymer itself, by opposition to impurity states [WIN 03]. Here, a powerful tool was found in molecular simulation. As we saw in the first part of this chapter, it is perfectly possible to foresee the electrical properties of a given physical or chemical defect of a polymer chain, and in particular to define its propensity to stabilize an electron or a hole. More refined calculations can inform on the polarization of the medium generated by the charge, thus giving effective trap depths, which can be larger than estimated without consideration of conformational rearrangements.

3.4.4. Degradation induced by a charge and/or a field

This question is marginal with respect to the scope of this chapter, which has focused on the simulation of transport. We have, however, underlined in the introduction that the development of accurate models based on established physical approaches are needed. These models put down their roots in transport models, because factors of influence in the ageing are the local values of charge density or field, whatever the electrical ageing scenario considered. A local field would control the generation probability of hot carriers [ZEL 84] or the electromechanical strain of the medium [LEW 96]. A local charge density would control the irreversible evolution probability of the entities stabilizing these charges and involved in the ageing [DIS 01], as well as the recombination rate of charges in connection with chemical degradations (through electronic excitation of the recombining centers) [LAU 99]. Among relevant and promising simulation activities, we can distinguish two different areas pertaining to macroscopic and microscopic scales. A good example of the macroscopic approach of the problem is proposed in [MAZ 05]. Here, the molecular simulation has a strong added value. The chemical degradations induced by impact of carriers or by recombination of charges involve excited states of electrons or atoms. Simulations on chemical interactions made by Stoneham *et al.* [STO 01] show that in the excited state, the polymer chains evolve in time, through simple vibrations or rotations, or, in a more expected way, can even break. Thus, the excited states in the polymer can give rise to chain scission or radical recombination phenomena (see also [SAN 93]). These processes compete with energy relaxation in the form of light or heat. Molecular simulations of the excited states of the recombining centers deserve to be made. In a similar way, an understanding of the conformational changes associated with charge trapping could go through molecular simulations and be a way to study the steps from free volume formation to that of meso-voids, micro-voids, etc. This field is practically unexplored in the insulating polymers domain, and could be a way of improving the performances of insulators by controlling their molecular architecture.

3.4.5. *Contribution of the physics of non-insulating organic materials*

We have, essentially, been interested so far in insulating polymers. However, in support of the description of different mechanisms at work, we have resorted to research concerning semi-conductor materials, doped polymers and/or ionic conductors. It is very conceivable that the same set of mechanisms could apply to different classes of materials: the problem is to determine the relative importance of these different mechanisms. This is particularly delicate in the case of insulators which, unlike other materials, are not optimized, except for their not very conductive character from a macroscopic point of view and, in certain cases, by the orientation of their dielectric permittivity. An important fact here is the existence of scientific problems and common techniques for different classes: for example, in the case of organic electroluminescent devices, the common worries with insulators are the poor definition of the interface mechanisms, the influence of the space charge on behavior, the understanding and management of degradation under electrical stress. Further, most organic semi-conductors are more similar to insulators than to inorganic semi-conductors: with a relatively large band gap (2 eV and more), and transport controlled by *hopping* rather than according to a band mobility [WAL 02]. In the same way, we should be inspired by what was learned from the transport in ionic conductors to approach the case of insulators. This, therefore, provides a large scope to establishing physical bases common to different classes of organic materials.

3.5. Conclusions

Although the nature of conduction processes in insulating polymers is still a controversial subject, it appears to us that all the conditions – concerning the comprehension of mechanisms, multi-scale simulation approaches, numerical techniques, development of advanced characterization techniques – are available to develop transport and degradation models from different angles of the physics of phenomena. The use of electrical, physical and chemical characterization techniques, with good sensibilities and spatial and temporal resolutions, must be encouraged to tackle fundamental problems and determine the relevant physical parameters to incorporate into the meso and macroscopic models. Finally, molecular description has a high application potential in this field and must be developed in order to better capture the consequences of chemical and/or physical defects on charge stabilization in their environment and on the connection between charge transport, trapping and degradation mechanism – this latter point involving reconfigurations of chains and/or excited states.

3.6. Bibliography

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