A Review of Thermo-Stimulated Current

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Abstract

Thermo-stimulated Current (TSC) spectroscopy is widely used for studying insulating materials.
According to the structure, microstructure and morphology of a sample, TSC peaks must be described by various formalisms: The dielectric constant is given either by a power law of time/frequency or by a generalized Debye equation with a continuous or discrete distribution of relaxation times. Examples of the identification of TSC peaks with ionic or molecular movements are given.

Intoruction

Activated processes can be excited with a chemical stimulus - vapor stimulation [1] - or a physical one-photostimulation [2,3] and thermo-stimulation [4-6].

In the present paper, only techniques using a thermal stimulation will be discussed. In particular, a special attention will be paid to the Thermo-stimulated Current (TSC) technique.

The characteristics of this technique will be compared with those of the other thermally-stimulated spectroscopies. Then, the origins of TSC will be briefly cited.

Finally, examples of data obtained on inorganic and organic materials will be given.

I . Thermally-stimulated Methods

Among the wide variety of thermally-stimulated methods, we will now focus on the one based on the measure of photons or electrons during thermal stimulation.

TSC has been widely used for performing a rapid characterization of materials.

A) Thermoluminescence. (TL)

The sample is heated after having been exposed to various irradiations (X-rays, γ irradiation, particlebombardment, ultraviolet light). Energy is emitted as light during the heating. Many papers have been published reproting trap depths. In order to get more information, simultaneous measurements are usually performed by different thermally-stimulated techniques [7-14].

B) Thermally-stimulated electron emission (TSEE)

After having been exposed to irradiation at low temperature as in TL experiments, the sample is polarized by an electric field applied to the electrodes.
During the heating, the electron emission is recorded.
This TSEE technique allows the collection of the emitted electrons.
Note that only the surface of the sample is scanned [15-16].

C) Thermally-stimulated conductivity (TS Cond.)

With this method, a sample pressed between two electrodes is first excited at low temperature. TS Cond. measurements are usually made at constant electric field with a linear heating rate. The current is then recorded as a function of temperature [17-20].

The thermally-stimulated capacitance (TS Cap.) techniques are well adapted to the evaluation of the amount of deep level impurities, the hole thermal emission rate and the activation energy [12-23].

D) Thermally-stimulated polarization (TSP)

The sample is cooled down under short-circuit conditions and an electric field is applied. If the temperature is raised, then a current is measured versus time and temperature [24,25]. Numerical calculations of TSP curves have been carried out taking into account the temperature dependence of equilibrium polarization [26-28].

E) Thermo-stimulated currents (TSC)

The TSC technique involves the polarization of the sample by a static field at high temperature. The sample is then cooled to a temperature at which the external field is removed and warmed at a constant rate. A current corresponding to dipole relaxation is recorded as a function of time and temperature. The obtained results may be compared with those supplied by other conventional techniques [29-31].

II. Thermo-Stimulated Currents (TSC)

Various experimental TSC apparatus have been described in the literature [32-34]. At the same time, a lot of criticism has been expressed because of the complexity of establishing non-isothermal theories [35-38].

In order to facilitate the analysis of TSC spectra, some particular experimental procedures such as a hyperbolic heating rate, have been proposed [39-41].

The analysis of the results will depend on the nature of the polarization orginated by the TSC current.

A) Orientataional polarization

This phenomenon occurs in the materials that contain molecular or ionic dipoles and depend on the part of the interaction of the dipoles with their surroundings, which can be represented by an effective viscosity. In molecular compounds, it is attributed to the restricted rotation of the whole molecule or of a part of it. In ionic crystals, it is associated with ions jumping between neighbouring sites (ion-vacancy pair). The criteria that have been adopted to identify the great number of dipolar relaxation phenomena are the following:

- the proportionality of the TSC response with the polarizing field,
- the independence of TSC with the electrode - sample interface.

In general, the TSC spectra are complex. Two kinds of analyses have been proposed:

- the complex TSC spectra are described in the hypothesis either of a continuous distribution of relaxation time [42,43], or of the universal dielectric response of Jonscher [5,44,45].
- the complex spectra are experimentally resolved into elementary processes using fractional polarization techniques [46-50].
  Each elementary process is characterized by a single relaxation time. These relaxation parameters have been correlated with other chemical or physical ones [51-55].

B) Space change polarization

In this case, the polarization is due to the presence of excess charge carriers (electronic or ionic). A macroscopic charge transfer is observed between the electrodes. The origin of those charges can be intrinsic (heterocharges) or extrinsic (homocharges).

This polarization phenomenon is more complex than the dipolar one because it depends on a great number of parameters.

In order to describe the space charge mechanisms, two basic models have been proposed:

- the exchange transport model, in which the conductivity of the material plays an important role [56-65].
- the trapping model, where the nature of the traps is essential[66-68].

C) Interfacial polarization

In heterogeneous polymers', space charges tend to pile up near the interfaces between zones of different conductivities. This well-known phenomenon is called the Maxwell-Wagner-Sillars effect (MWS).
It plays an importantrole in the polarization of composites [69,70].

Ⅲ. Inorganic Materials

A) Insulators

1. Halide crystals

Alkali halides have been among the first crystals studied by TSC [71-73]. Non-linear polarization phenomena interpreted in terms of ionic space charge have been studied [74-76]. Thoses studies generally concern dipolar polarization. Simple atomic models have been developed; they allow the prediction of defect concentrations [77-97].
The precipitation of impurities induces dipolar aggregates, which appear to follow third order kinetics [98-101].

Many works have also been carried out on alkaline earth halides [102-106] such as fluorine CaF_2 [107-111].
Recently, the dielectric properties of some solid solutions have been studied [112-117].

Other halide crystals have been centered on mercuric iodide, which is believed to present some interest for low energy γ ray detection [121-124].

2. Other crystals

In more complex crystals, space charge polarization phenomena are observed [125-133]. For example, a TSC study of $AgGaS_2$, which is of particular interest for non-linear optics applications, has allowed the characterization of deep traps [134,135]. On the other hand, the existenc of stable - metastable phase transitions accompanying dipolar relaxation mechanisms has been confirmed [136,137].

As for the ferroelectric crystals, the influence of defects on phase transitions has been studied in barium titanate [138,139], ammonium sulfate [140], and its derived products [141-144].

3. Polycrystal

a) *Ice* - The dielectric study of polycrystallineice [145,146] or of dispersion of ice microcrystals [147] has shown the existence of a low temperature relaxation mode due to dipolar absorption in ice. Moreover, a high temperature peak has been associated with space charge relaxations characteristic of morphology.

b) *Ceramics* - Ceramics systematically exhibit non-ohmic space charge effects [154-156].

4. Amorphous

In amorphous insulators, the resolving power of TSC has enabled new results to be optained [154-156].

a) *Inorganic glasses* - The study of the dielectric properties of glasses appears to be difficult because of the simultaneous presence of localized motions of alkaliions and delocalized migration phenomena [157-165].

b) *Electronic insulators* - Special attention has been paid to the insulators used in the electrical industry. So, silicone resins that might have potentional applications as thermoelectrets have been studied [166]. Specific works have also been devoted to silicon monoxide SiO [167-171], silicon dioxide SiO_2 [172-174], and SiO2 - metal interfaces [175-187].

Others structures, such as metal-oxide-semiconductor (MOS) structure [118] or metal-nitride-oxide-semiconductor (MNOS) [189], have been characterized.
Finally, TSC measurements have been performed on p-n junctions for determinning the impurity-center parameters [190-195].

B) Semiconductors

1. Crystals

In monocrystalline selenium films, traps have been investigated using TSC spectroscopy [196]. Intensive research has been devoted to developing cadmium telluride CdTe crystals [197-200], in particular for room γ-ray detectors. Differentmethods of analysis have been proposed, including those taking into account the retrapping of the carriers [197].

Inverstigations of trap parameters have been carried out on selenides [201], such as indium selenide [202-204], by using TSC. The literature reports also the trap parameters of gallium crystals [205-215] or thermally-stimulated conductivity studies [216-218].

2. Amorphous

There have been many stuides on amorphous selenium, since this material has become important for practical applications such as electrophotography [219-221]. Two relaxation modes have been isolated by the TSC technique:

- at about 0℃, a TSC peak is observed. It has been associated with a discrete trapping level and a field independent mobility;
- at low temperature, the field dependent peak is well described by the continuous distribution of thermally-activated hole drift mobility.

Since 1980, amorphous silicon has been the subject of many papers. The good photovoltaic performances obtained in diodes proved that this material is convenient for solar energy conversion [222-227].
In particular, these studies allowed the characterization of band tail states and levels due to impurities.

Original results have been obtained by TSC on different semi-insulating amorphous materials [228-231].
Arsenicselenide is then a hole-conducting material near room temperature with a Fermi level situated near the valence hand [232-234].

Ⅳ. Organic Material

Most of the papers on organic materials are devoted to macromolecules. However, some interesting results have been obtained on small molecules.

A) Small molecules

1. Non-crystalline state

The TSC technique has been applied successfully to the study of some liquids constituted of complex organic molecules, urea type [235], or to the study of polar liquids such as alcohols [236,237]. For example, the study of a series of cycloalcohols has shown the existence of a "glass crystal"[238].

It has been noticed that aromatic hydrocarbons like tetracene tend to form amorphous films when deposited at low temperature. A TSC characterization has displayed that the dielectric properties of the films depend stongly on their amorphous structurer [239].

Abietic esters are of particular interest for photothermoplastic devices used in holographic optical switching. Using the TSC techniques, correlations between structure and properties have been carried out on these amorphous materials [240,241]. Note that crystalline domains have been also characterized in oligomers [242].

2. Crystalline state

In organic semiconductors such as anthracene [7,243-250] perylen[251] and β metal free phthalocyanine [252], discrete hopping levels have been observed. Because of their analogies, they could have a common physical orgin.

B) Macromolecules

1. Synthetic macromolecules

In this section, the presentation of amorphous and semi-crystalline polymers will be followed by a study of the specific problems encountered in copolymers, blends and composites.

• *Polyethylene terephthalate* (PET) - One of the difficulties encountered in PET studies is to distinguish the various regimes of polarization [288-292]. By using TSC measurements with the contact and contactless electrodes, three kinds of charges have been observed[293]:
- a heterocharge due to dipole orientation,
- a heterocharge due to ionic charge drift,
- a homocharge with extrinsic origin.

In PET, most of the papers are devoted to the space charge mechanisms [294-300]. Dipolar relaxation studies show the existence of a sub-Tg mode with three sub-modes that have been characterized [301-305].

• *Poly-p-phenylene sulphide* (PPS) - There have been extensive studies on PPS films that give highly conducting complexes with various electron acceptors.
The conductivity of PPS films increases by doping with organic acceptors as well as inorganic ones [306].

• *Polycarbonate* (PC) - Since polycarbonate is well known for its ultimate mechanical properties, TSC studies have been carried out for exploring its microstructure [307-314]. The existence of a "granular structure" with ordered domains embedded in the "true" amorphous regions has been confirmed.

• *Epoxy resins* - Because of their good mechanical properties, expoxy resins have encountered a great success. The TSC study of the "low temperature" relaxation modes has given complementary information on the molecular motions of the networks [315-318]. In fact, TSC is well adapted to the characterization of the influence of thermal treatments [316-317]. Epoxy resins have good adhesive properties, too. The analysis of the peaks due to space charge polarization and to interfacial polarization allows the investigation of the interface [318]. The properties of epoxy resins have also been studied by varying stoichiometric ration [319].

b) Semi-crystalline polymers - The TSC spectra of semicrystalline polymers are more complex than those of amorphous polymers [302]. An additional peak, located in the vicinity of the melting and named α, is observed.
For polymers having a super-structure, the relaxation mode associated with the glass transition, β, shows the existence of two components.

a) Amorphous polymers - The characteristics of the TSC spectra of amorphous polymers are the following:

- Below the glass transition temperature, Tg, the TSC peaks are generally due to the orientation of dipoloes.
  The "primary" relaxation mode, which is the most intense, is located in the vicinity of the glass transition; it is designated by α; the "secondary" relaxations are named $\beta, \gamma, ...$, in the order decreasing temperatues. The α mode involves cooperative motions of sequences of main chains of about 25Å, while the $\beta, \gamma, ...$ are due to more localized movements of small entities [253-255].

- Above Tg, delocalized movements all along the main chain and space charge phenomena appear. Their intensity depends on the experimental conditions [256-262]. For this reason, this part of the TSC spectrum is particularly difficult to investigate.
  Now, let us mention some data concerning typical polymers:

- *Polymethyl methacrylate (PMMA)* - Many studies have been deveted to dipolar relaxation modes of PMMA [263-269]. The β relaxation mode of this material corresponds to local motions of side chains.
  The study of the influence of tacticity on the relaxation modes [270,271] has confirmed the hypothesis proposed by different authors to explain the origin of these modes. If there is an agreement on the origin of the TSC peaks located below Tg, those situated above the glass transition have given rise to much controversy. Indeed, some authors relate these high temperature peaks to the dielectric manifestation of the "liquid-liquid" transition, while others attribute them to a space charge polarization.

- *Polystyrene* (PS) - Like PMMA, the super Tg peak has provided a subject of controversy on its molecular origin [276-278]. PS is often chosen as a model polymer [279-281] or as an "electret"[282]. There are studies of doped PS films [283,284], and some interesting results obtained on the complex of polystyrene sulfonic acid films (PSSA) with various degrees of sulfuration has also been examined by TSC.

Most of the polymers are insulators. Nevertheless, the novel electric properties observed in polyacetylene have inspired an increasing amount of interest [321].
This highly crystalline polymer needed a technique with a high resolving power like TSC to study the molecular motion associated with its glass transition [322-324].

Polyolefins:

- *Polyethylene* - Polythylene, which is the simplest polymer because of its chemical formula, is probably the most difficult to characterize. Thereby, the problem of the reproducibility of the TSC spectra is still unresolved. The space charge mechanisms have been widely investigated in high density polythylene HDPE [325-335] as in low density polythylene LDPE [336-347]. The characterization of the processes of dipolar re-orientation is difficult [348-356]. On the other hand, spectacular compensation phenomena have been observed for the β and α relaxation modes.

- *Polypropylene* - This polyolefin behaves differently from the preceding one [357-365]. Here, the dipolar relaxation phenomena associated with the glass transition are easier to identify. The data obtained has been the basis of a hypothesis of the existence of two amorphous phases:

- the interspherulitic amorphous phase, free from stress, corresponds to the "lower temperature component, "Tg", of the glass transition;

- the intraspherulitic amporhous phase, restrained by the crystallites, is reponsible for the "upper temperature component", "Tg" of the glass transition.

Polymers with hydrogen bonds: TSC studies of polyamide 66 [47,366-368], polyamide 6[369,370], and polyamide 12 have been carried out. In addition to these industrial aliphatic polymers, some model aromatic polymers [373] have been characterized and compared to polysulfonamides [374,375].

It is interesting to note that the most spectacular compensation laws have been observed in polyamides.

They show the existence of a "structured" amorphous phase stabilized by hydrogen bonds.

Halogen-containing polymers: According to their chemical composition, theses polymers are amorphous, like polyvinylchloride PVC[376-378], or semicrystalline, like polyvinylidene fluoride PVDF and polytetrafluoroethylene PTFE.

- *Polyvinylidene fluoride* - One of the most extensively studied halogenous polymers is PVDF because of its interesting piezo and pyroelectric properties. The properties of PVDF have been reported to depend upon the crystalline phase. A comparative study of the non polar α and β phases has shown that a change of the phase is accompanied by a structural change in the amorphous region and in the amorphous-crystalline interphase.

- *Polyternfluoroethylene* - The polymer showing the best charge transfer properties is PTFE [396-398].
  TSC studies have reported a pyroelectric effect.

- *Polychlorotrifuoroethylene* - TCTFE with relatively low crystallinity has been characterized by TSC. Four relaxation processes have been found to occur in the crystalline or in the amorphous phases [399,400].

Copolymers and blends:

- *Copolymers* - In general, the aim of copolymerization is the improvement of the properities of parent homopolymers. So, one of the best electrets is obtained with the fluorinated ethylene propylene copolymer FEP [401-405].
  Different kinds of copolymers[406-418], salts of copolymers[419,420], and terpolymers [421-424] have been investigated using the TSC technique. The primary purpose of these studies was the evaluation of the compatibility of the different phases.

- *Blends* - In some blends, the analysis of TSC peaks does not lead to final conclusions [425]. In other blends, on the contrary, interesting results are obtained [426-428]. One of the most significant conclusions is the introduction of the concept of polymer miscibility depending upon the considered scale : it might explain several apparent discrepancies in the literature [429-430].

Composites: The importance of composite materials in the electrical industry is increasing because of their good long-term performance. So, better understading of their characteristics in necessary.

It is now well-known that the physical properties of composites depend on the nature of the interface/interphase. TSC studies have been devoted to composites containing insulating fillers.

The two different classes of polymer matrices-thermosets[69,431-436] and thermoplastics[437-440] have been considered. From TSC analysis, a number of assumptions have been made about the properties of the interface:

- modification of the dipolar orientation polarization associated with the creation of bonds, which induce a modification of the matrix;
- appearance of an interfacial polarization due to heterogeneities of the electric conductivity [433,441].

However, this interface is no longer regarded as a sharp boundary but is now considered to be an "interphase". i.e. a region surrounding the filler where properties differ from those of the buik matrix.
Its characterization remains a largely unsolved problem. The influence of the interphase on the dielectric properties of model composites has been studied by TSC in reference [442].

Natural macromolecules : These macromolecules are classified according to their origin.

- *Macromolecules from the vegetable kingdown* - Simple macromolecules like amylose[443] and pullulan[444-445] have been studied by TSC. For more complex macromolecules like cellulose[446-50], the information is macroscopic. The characterization of these polymers in the hydrated state is difficult.
  Nevertheless, studies of the water-cellulose interactions have given interesting data: In the low temperature region, water acts as an anti-plasticizer, while in the high temperature region, it acts as a plasticizer [451].

• *Macromolecules from the aminal kingdom* - The TSC technique has been used to perform a detailed study of the most important a minoacids. Besides punctual studies of macromolecules[457-461], some extensive research has been carried out. So, the TSC spectrum of elastin has been indexed in correlation with a detailed analysis of the most characteristic triand penta-peptidic sequences [462].
Special attention has been paid to collagen [463-468].
The dipolar relaxation spectrum has been completely characterized from the localized movements of the α chain sequences to the relative motions of tropocollagen macromolecules.
Calcified tissue, which can be considered a natural composite, has also been studied by TSC. First, a previous study of the apatitic mineral phase has been performed. Because of the complexity of these materials, synthetic models have been used [464,469-475] before studying natural phosphaes[476-478]. Owing to the results obtained on the mineral and organic phases, the role of the interfaces in calcieied tissues has been characterized [477,479].

Conclusion

This review illustrates the various areas of application of Thermo-stimulated Current spectroscopy. It has been widely used for performing a rapid characterization of materials, and TSC spectra are often compared with differential scanning calorimetry spectra. In industrial laboratories, it can be used for qualifty control of insulations. When TSC is coupled with relaxation map analysis, it is involved in fundamental investigations of the molecular origin of dielectric lossesl. It is also interesting to calculate dielectric surfaces as a function of temperature and frequency. This kind of information might be particularly helpful in the research of insulators for drastic environmental conditions.

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