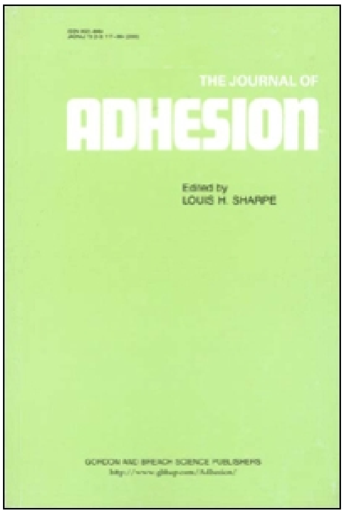

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Characterization of Boundary Phenomena Using Broadband Dielectric Spectroscopy*

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Applicability of low-frequency dielectric methods of investigation of solid inhomogeneous structures are presented. The methods prove to be very useful for determination of physical properties of both inhomogeneous one-component and multi-component systems including systems arising as a result of adsorption of gases and liquids onto solid surfaces. It is also possible to study adhesion of composite components using the dielectric methods. The methods are particularly useful for investigations of ageing phenomena of polymer composites. The dielectric properties of two polycrystalline low-molecular weight organic compounds are presented as an example of investigations of one-component inhomogeneous structures.

Keywords: Low-frequency dielectric properties; broadband dielectric measurements; organic polycrystalline structures; inhomogeneous systems; polymer composites; water ageing

1. INTRODUCTION

A remarkable interest in the physical properties of one-component and multi-component inhomogeneous structures has been developed in the recent years. In particular, this refers to polymer composites that are widely used for many technological applications. It was discovered that

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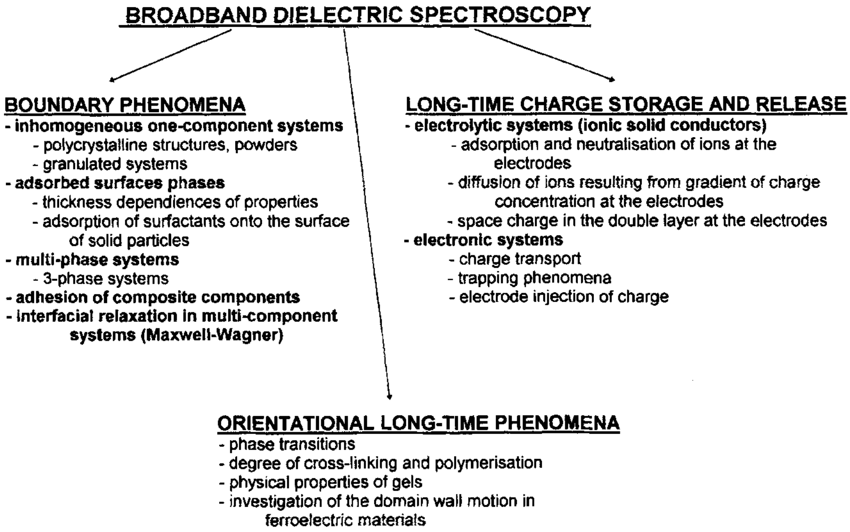
*One of a Collection of papers honoring Yuri S. Lipatov on the occasion of his 70th birthday, 10 July 1997.

the adhesion between the components determines to a large extent their properties. The role of interfacial phenomena in polymer blends was very soon discussed, analyzed and deeply described by Lipatov [1, 2]. It has been shown that we have to deal with an interface and an interphase. There are very many techniques which are at present used to characterize the interface between two or more components of the system (blends and various filled polymers). Among the methods used for investigations of the physical properties of multi-phase systems broadband[1] dielectric spectroscopy (BDS) is less often used but it deserves special attention [3]. It will be shown in this paper that the applicability of BDS for investigation of inhomogeneous one-component and multi-component systems is very wide. In this situation, it seems reasonable to present briefly the general applicability of BDS.

In general, three basic groups of research problems can be enumerated for which the BDS may be used (see Fig. 1), namely boundary phenomena, long-time orientational phenomena and long-time charge storage and release.



BROADBAND DIELECTRIC SPECTROSCOPY

BOUNDARY PHENOMENA

- **inhomogeneous one-component systems**
  - polycrystalline structures, powders
  - granulated systems
- **adsorbed surfaces phases**
  - thickness dependiences of properties
  - adsorption of surfactants onto the surface of solid particles
- **multi-phase systems**
  - 3-phase systems
- **adhesion of composite components**
- **interfacial relaxation in multi-component systems (Maxwell-Wagner)**

LONG-TIME CHARGE STORAGE AND RELEASE

- **electrolytic systems (ionic solid conductors)**
  - adsorption and neutralisation of ions at the electrodes
  - diffusion of ions resulting from gradient of charge concentration at the electrodes
  - space charge in the double layer at the electrodes
- **electronic systems**
  - charge transport
  - trapping phenomena
  - electrode injection of charge

ORIENTATIONAL LONG-TIME PHENOMENA

- phase transitions
- degree of cross-linking and polymerisation
- physical properties of gels
- investigation of the domain wall motion in ferroelectric materials

FIGURE 1 Scheme of possible applications of Broadband Dielectric Spectroscopy.

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[1] Nowadays dielectric measurements at ultralow frequencies down to 10^{-6} Hz may be carried out using commercially available equipment. In this paper, the range between 10^{-3} Hz–10^{6} Hz available with standard Solartron or Novocontrol broadband dielectric equipment will be discussed.

Boundary phenomena are the broadest group of problems of the mentioned above. The following research fields may be counted among the boundary phenomena:

- inhomogeneous one-component systems (polycrystalline structures including powders and granulated systems often used as adsorbents and sensors due to their well-developed surface) [4, 5]
- adsorbed surface phases of polar and non-polar molecules. A very important problem of surfactants adsorbed on solid surfaces should be mentioned at this point [6, 7]. Such investigations may be useful for pharmaceutical purposes [8]. Dielectric low-frequency measurements enable one to investigate the thickness dependencies of physical properties of adsorbed thin films [9, 10].
- multiphase systems with special reference to 3-phase systems originating when air humidity is absorbed into 2-phase composite materials.
- adhesion of composite components. As a result of ageing phenomena the adhesion between the polymer matrix and the filler may be partially destroyed giving rise to poor mechanical properties. Low-frequency dielectric measurements may be used as a non-destructive method of detection of the changing adhesion of composite components resulting from water ageing.
- interfacial dielectric polarization (Maxwell-Wagner-Sillars) may also be detected.

Orientational long-time phenomena are not a subject of this paper. Let us mention that it is possible to investigate the phase transitions in high-molecular organic compounds [11, 12], the degree of cross-linking and extent of polymerization [13, 14], the physical properties of gels [15, 16] and the domain wall motion in ferroelectric materials [17].

Long-time charge storage and release may occur both in ionic solid conductors and in conducting systems predominated by electronic transport. In the case of the ionic conductors a few research problems may be a subject of investigations [18, 19], namely the adsorption and neutralization of ions at the electrodes, the diffusion of ions resulting from the gradient of charge concentration at the electrodes and the space charge in the double layer at the electrodes. Besides, a strongly dispersive behavior called Low Frequency Dispersion has been detected in some solid ionic conductors [20–21]. This kind of dispersion at low frequencies is considered to be due to bulk phenomena.

As far as the systems predominated by electronic transport are concerned it is possible to investigate the mechanism of charge transport, the trapping phenomena and the injection of charge from electrodes [23–26].

As we see, a great variety of phenomena may be investigated by BDS and to show the broad applicability of this technique is one of the purposes of this paper. However, the main subject of this paper is to discuss concisely the boundary phenomena in solid inhomogeneous systems mentioned above. Detailed discussion would make this paper overly long, so only one typical example illustrating the various boundary phenomena enumerated in Figure 1 will be presented.

The dielectric response of materials can be described by the complex capacitance:

$$C^*(\omega) = C' - iC'' = C(\omega) - iG(\omega)/\omega = G_f(\varepsilon' - i\varepsilon'') \qquad (1)$$

where $C(\omega)$ is the electrical capacitance, $G(\omega)$ is the conductance, ε' and ε'' are the real and imaginary parts of the dielectric permittivity and G_f is a geometrical factor. As we see, the spectral shape of the $C(\omega)$ and $G(\omega)/\omega$ curves is identical to the shape of the $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$ curves so it is possible to present the dielectric data in log $C(\omega)$, $G(\omega)/\omega$ *vs.* log ω form.

Taking into account the specific character of this paper, the detailed description of experimental techniques will be omitted. In general, the use of BDS consists in determination of the current response of a system to a sinusoidal applaied voltage. The construction of a sample cell varies according to the substance and effect which is to be measured. The polycrystalline samples of simple aromatic hydrocarbons were obtained by evaporation in vacuum under a pressure of the order of 10^{-5} Torr. The metal (mainly gold) electrodes were also evaporated in vacuum. The measurements were carried out using a Solartron Frequency Analyzer with Chelsea Dielectric Interface.

2. BOUNDARY PHENOMENA

2.1. One Component Systems

Polycrystalline structures including powders and other granulated materials are often used as adsorbents or gas sensors due to their well-developed surface. Some aspects of adsorption on solid surfaces will be discussed later. At this point, we shall discuss briefly the influence of structural inhomogeneities on the dielectric properties of polycrystalline systems.

Powders and non-oriented polycrystalline layers consist of small crystalline grains which show directional disorder of the crystal axes. It may be expected in such cases that there exists some intermediate region between the crystalline grains containing a more disordered substance. The physical properties of the intergrain substance should differ from the properties of the crystalline material inside the grains. If we assume that there is no absorption from the environment to the intermediate regions, then in the case of a polar substance the intermediate, more disordered, regions should just give rise to an additional broadening of the dielectric loss peak. The broadening results from greater statistical disorder of the intermolecular interactions in the less-perfect intermediate regions. The classical Maxwell-Wagner relaxations may also be expected in this case.

Much more interesting situations arise when the dielectric response is determined by movement of semi-free charge carriers in carrier-dominated systems. The investigations of the influence of the structural inhomogeneities on the dielectric properties of carrier-dominated systems have been carried out for *p*-terphenyl small-grain and large-grain polycrystalline structures [26, 27]. Figure 2 shows the dielectric response of a small-grain polycrystalline *p*-terphenyl film. The G/ω curve consists of two main parts. At the higher frequencies the slope of the curve is equal to about -0.2 which corresponds to n close to 0.8 in the power law:

$$G(\omega)/\omega \propto \omega^{n-1} \tag{2}$$

The activation energy of this part of the G/ω curve is rather low, of the order of 10^{-2} eV (see Fig. 3). This part of the dielectric response may be interpreted as a hopping transport of charge carriers among the states localized in a narrow band of states at the Fermi level [25]. The low frequency part of the G/ω curve is well described by the power law with n close to $+0.5$. It has been shown by a computer simulation that the spectral shape of the dielectric response of a hopping system, predominated by difficult transitions related to the inter-grain barriers, may be

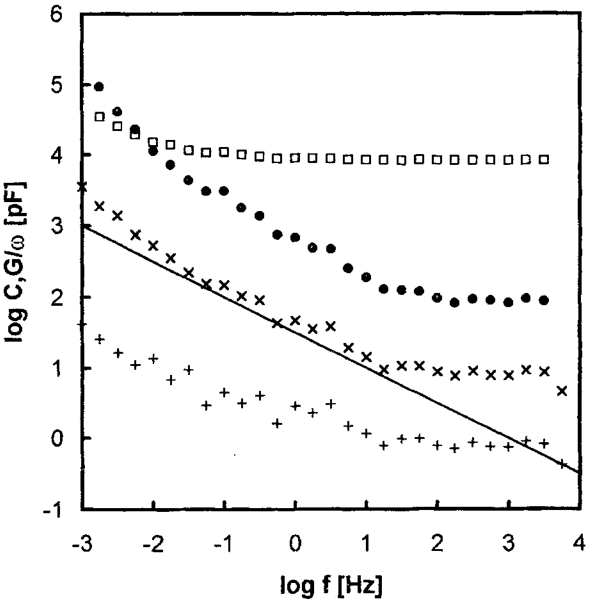

FIGURE 2 Dielectric response of *p*-terphenyl small-grain polycrystalline film. G/ω: + 230 K, × 250 K, ●270 K. □ C at 270 K. The points for 230 K are at their right place. The other curves are shifted up by 1 order of magnitude to each other to avoid overcrowding. The slope of the solid line equals −0.5.

described by the power law with n close to −0.5 [28]. The above interpretation is the more justified as:

- the activation energy of the low frequency part of the G/ω curve is by about one order of magnitude greater than the high frequency one.
- the low frequency dielectric response described by n close to 0.5 has not been detected in the large-grain films. The size of grains in these films is not smaller than their thickness, so the charge carriers do not scatter at the inter-grain barriers on their way from one electrode to the other.

The activation energy of the lowest frequencies resulting from Figure 3 (equal to about 0.2 eV) may be interpreted as the energy of scattering of charge carriers with the inter-grain barrier originating at the inter-surface region of contact of two grains. The results presented about show that the broad band dielectric measurements enable one

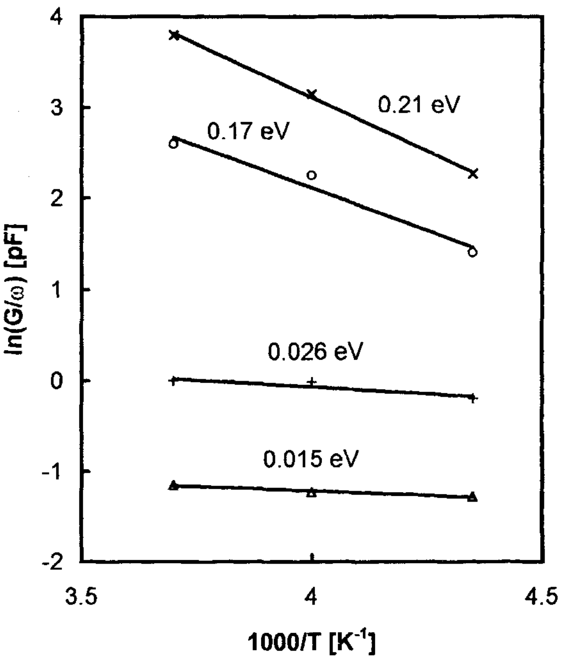

FIGURE 3 The temperature dependence of the imaginary part of dielectric capacitance G/ω at various frequencies. Δ1000 Hz, + 100 Hz, °0.316 Hz, × 0.0316 Hz. The points corresponding to 1000 Hz are shifted down by one order of magnitude to avoid overcrowding.

to investigate both the physical phenomena inside the grains (by measuring the dielectric response at high enough frequencies) and the interaction of charge with the structure inhomogeneities (by measuring at low enough frequencies).

Very similar results have been obtained for polycrystalline tetrabenzofulvalene (TBF) thin films (see Fig. 4). In this case, the activation energy changes from 0.045 eV at 10^4 Hz to 0.28 eV at a frequency of 0.1 Hz (Fig. 5). The distance travelled by charge carriers during half the period of a sinusoidal electric field depends on the frequency of the field and on its amplitude. This distance in *p*-terphenyl films becomes equal to the average diameter of grains at about a few tens of hertz (taking typical values of the drift mobility $\mu = 10^{-9}$ m^{2}V^{-1}s^{-1} [29], the amplitude of the measuring field $V_0 = 2V$, the sample thickness $d = 4$ μm and the average diameter of grains $d = 2$ μm (see Fig. 6)).

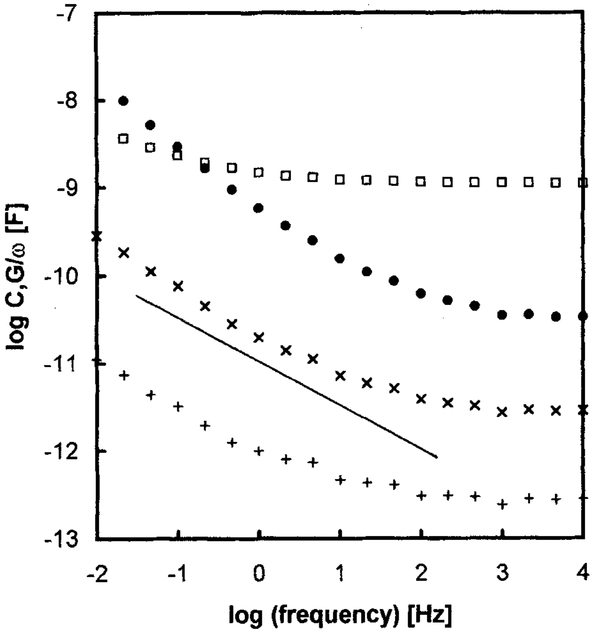

FIGURE 4 Dielectric response of TBF polycrystalline film at various temperatures. G/ω: + 300 K, × 320 K, ●340 K. C: □ 340 K. The points for 300 K are at their right place. The other curves are displaced by one order of magnitude up with respect to each other to avoid overcrowding.

This confirms that at frequencies below about 100 Hz the scattering in the inter-grain regions should have an outstanding influence on the dielectric response. It is not possible to estimate the value of the limiting frequency for TBF polycrystalline films as the mobility measurements have not been carried out. However, the increasing value of the limiting frequency with temperature (see Fig. 4) may be considered to be an indirect proof suggesting the influence of the inter-grain regions at the low frequencies.

2.2. Composite Materials

2.2.1. Three-phase Systems with Electrolytic Interphase

The importance of composite materials and polymer blends in science and technology has increased significantly durign the last 20 years and

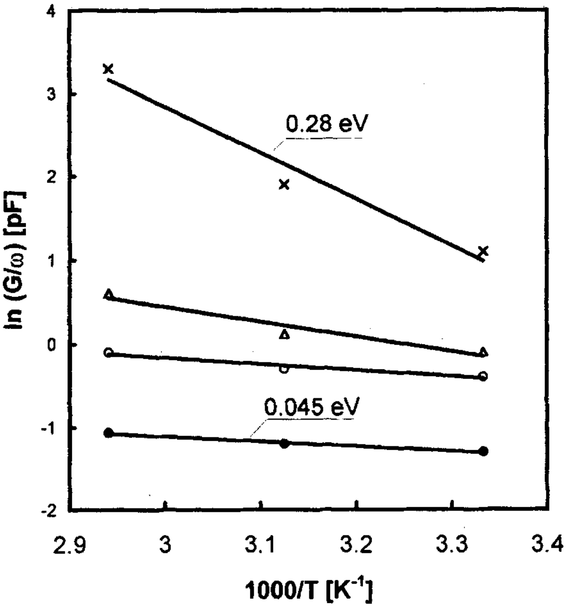

FIGURE 5 Temperature dependence of G/ω in polycrystalline TBF films at various frequencies. ● 10^4 Hz, o 10^3 Hz, Δ 10^2 Hz, × 0.1 Hz. The curves at 10^4 Hz and 0.1 Hz are at their correct place. The two other curves are displaced up by one order of magnitude to avoid overcrowding.

further increase of interest in these materials may be predicted (see *e.g.*, [30, 31]). A particularly important feature of composite materials is their resistance to external conditions such as temperature, humidity, chemical agents, etc., because all these factors may influence the physical properties of the composite and give rise to its mechanical degradation and a change of its electrical properties. Application of BDS for investigations of the influence of humidity on the physical properties of polymer composites is the subject of this part of the paper.

Broadband dielectric measurements may be used both for estimation of absorption of water into a composite and for investigations of the influence of the absorbed water on the properties of the composite. In particular, the measurements may enable one to estimate the leaching of ions from the filler surface, the influence of treatment of the filler surface on durability of the composite the interaction of ions in the electrolyte originating between the filler and the matrix with the adhering filler/matrix surfaces.

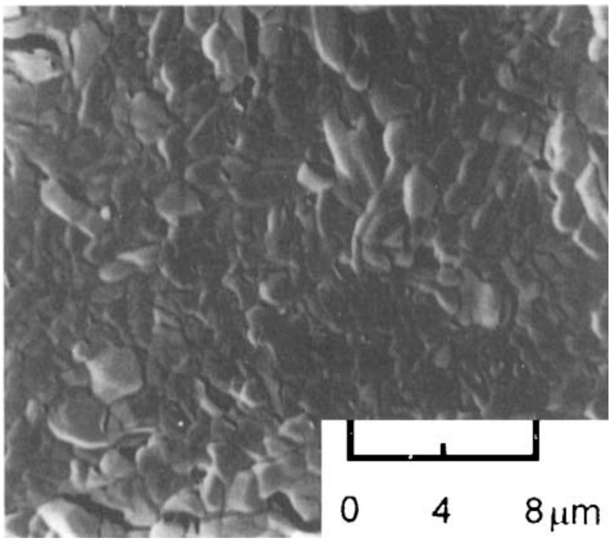

FIGURE 6 Electron micrograph of a typical polycrystalline *p*-terphenyl film.

Very convincing experiments concerning the absorption of water into polymer composites were carried out by Steeman, Maurer and others [32–35]. They chose glass bead-filled high density polyethylene as a model composite for their investigations. The glass filler volume fraction was 20% [32]. After one-year of drying, the samples were exposed to environments of various relative humidity. The dielectric measurements were carried out in the frequency range 0.1 Hz–31.6 kHz and in the temperature range $-70°C$ to 36°C. A dielectric loss peak dependent both on temperature and the relative humidity of environment (*i.e.*, on the amount of water absorbed into the composite) has been detected. The dielectric response of the composite has been described by Maurer's model, which foresees the following expression for the relaxation time, τ, of the loss process resulting from the existence of the electrolyte interlayer between the polymer matrix and the filler [35]:

$$\tau = \frac{3\Phi_f \varepsilon_{\mathrm{vac}}}{2(1-\Phi_f)\sigma_l \Phi_l}\{(\varepsilon_f + 2\varepsilon_m) - (\varepsilon_f - \varepsilon_m)\Phi_f\} \tag{3}$$

where ε_i $(i = m,f)$ are the matrix and the filler permittivities and $\varepsilon_{\mathrm{vac}}$ is the vacuum permittivity. σ_1 is the electrical conductivity of the interlayer, Φ_f

is the volume fraction of the filler, and Φ_l is the volume fraction of the interlayer. The experimental relationship between the frequency of the loss maximum and the temperature, $f_{\max}$, may be described by the Arrhenius relation:

$$\ln(f_{\max}) = \ln(f_0) - \frac{E_A}{kT} \tag{4}$$

where E_A is the activation energy, k is the Boltzmann constant and T is the temperature. On the other hand, the above relation resulting from Eq. (3) is of the form:

$$\ln(f_{\max}) = \ln(\mathrm{const}) + \ln(\Phi_l) + \ln(\sigma_l) \tag{5}$$

For a given volume fraction of the absorbed water we can assume that $\ln(\mathrm{const}) + \ln(\Phi_l) = \mathrm{const}$. In this situation, the temperature dependence of the thin layer conductivity is of the exponential form:

$$\sigma(T) = \sigma_0 \exp\left\{-\frac{E_A}{kT}\right\} \tag{6}$$

which is in a good agreement with the expression suggested by Fripiat and Jelli [36]. The activation energy may be regarded as a potential barrier to the moving ions. The potential barrier is related to the interactions of the moving ions with the surface of the filler covered with the double layer existing at the very large filler surface [34,35]. The experimental relationship between the activation energy and the relative mass gain (or the thickness of the interlayer electrolyte, see Fig. 7) enables one to estimate the amount of absorbed water and the thickness of the interlayer between the matrix and the filler if the activation energy of the peak frequency is known from the experimental results [32].

BDS and the models describing the three-phase systems consisting of polymer matrix, filler and the electrolyte interlayer may also be used for investigations of the surface phenomena in water-aged composites and the influence of treatment of the filler surface. An example of such investigations has been presented by Steeman and Maurer [34]. A glass-bead-filled high density polyethylene (HDPE) composite with a

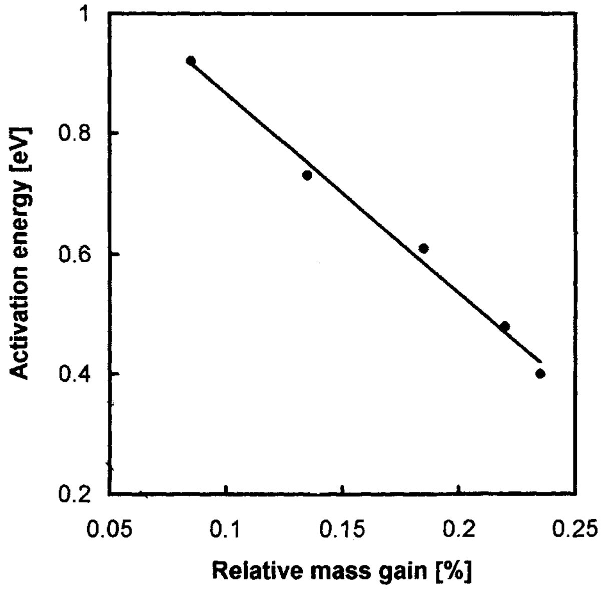

FIGURE 7 The activation energy of the detected dielectric losses as a function of the amount of water absorbed. Redrawn after [32].

modified surface of the filler was a subject of the investigations. The glass filler surface was modified by covering it with azidosilane layers of various thickness. The number of silane layers was between zero (unmodified filler surface) and five. Such composite samples were exposed to air environments of various relative humidities until equilibrium was achieved. The amount of absorbed water turned out to be dependent on modification of the filler surface. The greatest mass gain (*i.e.*, the greatest amount of absorbed water) took place at the two silane layers covering the glass filler. This results from the greatest surface of adsorption which also may be estimated by means of low frequency dielectric measurements [34]. The influence of the thickness of the silane layer is so strong that the mass gain for two monolayer silane layers at 31% relative humidity is very close to that for an unmodified surface of glass filler at 51% relative humidity.

BDS also enables one to gain deep insight into the interactions of the electrolyte interlayer with the modified filler surface [34, 35]. It has been shown that the peak frequency of the dielectric losses depends on the number of silane layers covering the glass filler for various relative humidities of the environment. According to Eq. (3) this may be either due to the different volume fractions (which the authors show is not the case) or to the different electrical conductivities of the two interlayers. Indeed, it has been suggested that the difference in electrical conductivity results from the strong interaction of water molecules with the modified filler surface [34].

2.2.2. Adhesion of Composite Components

Experimental data show that during water ageing of polymer composites water is often adsorbed into the composite between the matrix and the filler. If the adsorbed water can leach ions from the filler surface, this may lead to detaching the filler from the matrix. A good example of such a phenomenon has been presented by Bastioli *et al.* [3]. A glass fiber/polyethylene terephthalate composite was used for their investigations. The glass fiber was modified by covering with a silane epoxy. In order to compare the physical properties of the composite with both modified and unmodified glass filler, dielectric measurements in the frequency range 10^2 Hz – 10^6 Hz were carried out. The composites were aged in water at 87°C and 25°C (*i.e.*, below the temperature of the PET glass transition). An example of the results is shown in Figure 8. The dielectric measurements of the composites showed that there was no essential difference between dry PET and unaged composites with both modified and unmodified glass filler [37]. Besides, the influence of water ageing on the dielectric properties of the composite with modified glass filler turned out to be rather weak (see Fig. 8). However, the dielectric properties of the composite with the silane epoxy layer removed differs significantly from the properties of the modified composite. The reason for such evident differences between the properties of the two composites may be the different interaction between water molecules and the modified and unmodified surface of the filler [37]. In the case of the unmodified fibers the leaching of potassium oxide and sodium oxide from the filler surface takes place. According to the authors, the solute concentration was equal to about 2 M and the concentration was probably sufficient to enlarge the distance between the glass fiber and the PET matrix due to the osmotic pressure. Moreover, the alkaline solution is likely to enhance the dissolution of boron oxide from the fiber to form boric acid. The investigations of the unmodified glass fiber extracted from the aged composite confirmed the chemical attack on its

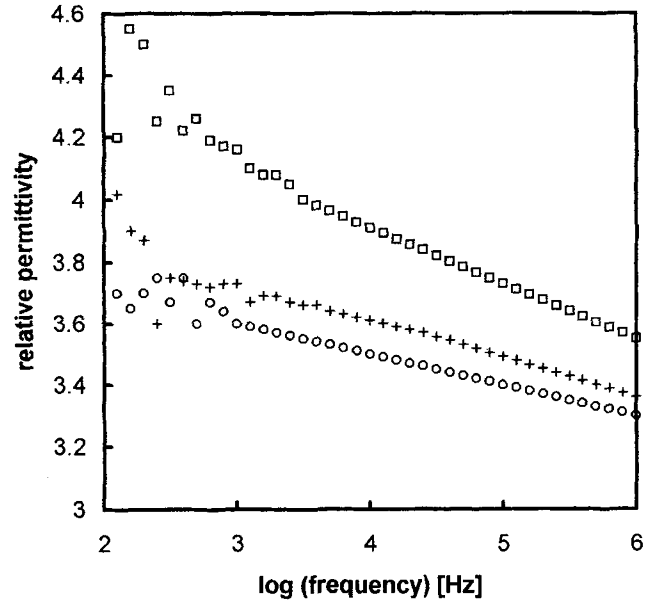

FIGURE 8 Permittivity as a function of frequency for PET (+), unmodified glass filled/PET composite (o) and modified flass filler/PET composite (□). The measurements were carried out after 30 days of ageing in water at 87°C. Redrawn after [37].

surface. On the other hand, electron micrographs confirmed that the distance between the glass fiber and the matrix in the unmodified aged composite was greater than in the modified one [37].

2.2.3. Maxwell-Wagner-Sillars Relaxations

If comparatively well-conducting particles are dispersed in some more poorly conducting environment then the so-called Maxwell-Wagner-Sillars (MWS) interfacial relaxation can occur. The peak frequency of the relaxations depends on the relationship between the conductivities and the permittivities of the conductive and the insulating part of the system and also on the shape of the conducting particles [38]. In the case of spherical inclusions the frequency of the loss factor maximum is given by [38]:

$$f = \frac{2\sigma_m + \sigma_i \times v(\sigma_i \times \sigma_m)}{2\pi\varepsilon_0 [2\varepsilon_m + \varepsilon_i - v(\varepsilon_i - \varepsilon_m)} \tag{7}$$

where ε_0 is the permittivity of free space, v is the volume fraction of the inclusions, σ_m, σ_i, ε_m and ε_i are the matrix and inclusion conductivities and complex permittivities, respectively (complex permittivity is given by $\varepsilon_m = \varepsilon' \sqrt{1 + \tan^2\delta}$, where ε' is the real part of the permittivity $\varepsilon^* = \varepsilon' - i\varepsilon''$ and $\tan\delta = \varepsilon''/\varepsilon'$ is the dissipation factor).

MWS relaxations have been detected in various dielectrics filled with highly-conducting fillers. These kinds of materials will not be discussed in this paper. There are also a lot of observations of MWS relaxations in polymer composites consisting of two components of slightly different conductivity (see, for instance, [39–41]). In general. it is possible to investigate the influence of a conductive filler on the electrical properties of a composite material. In particular, in the case of MWS polarization phenomena broadband dielectric measurements may be also used as a non-destructive method for investigating changes of the filler conductivity resulting from ageing phenomena, provided that no additional interphase between the two basic phases exists.

A good example of MWS relaxations has been published by Perrier and Bergeret [42]. Their research referred to glass-bead-polystyrene (PS) composites. The volume fraction of the glass filler was changed between 0–50%. The surface of the filler was not modified in any way, the measurements were carried out in the frequency range 20 Hz-1 MHz and for temperatures from room temperature to 553 K. Figure 9 shows the spectral shape of the imaginary part of the permittivity, $\varepsilon^* = \varepsilon' - i\varepsilon''$. The loss peak shown in Figure 9 has not been detected either in pure PS or in the glass. The authors analyze the peak frequency using Eq. (7) and find good agreement between theoretical predictions and their experimental results, though the agreement becomes worse for the higher volume fractions of the filler. This is not surprising if we take into account that the mutual interactions between the electrical dipoles arising in the glass inclusions increase with increasing filler volume fraction. Such a phenomenon has been also detected in other glass/polymer composites [41]. The authors show that BDS may enable one to detect the temperature dependence of the creep of the composite, though this may be detected by means of mechanical measurements, first of all. In this case the creep shifts to higher temperatures in comparison with pure polystyrene. The authors ascribe this phenomenon to the reinforcement effect of the charges induced at the filler/matrix interface.

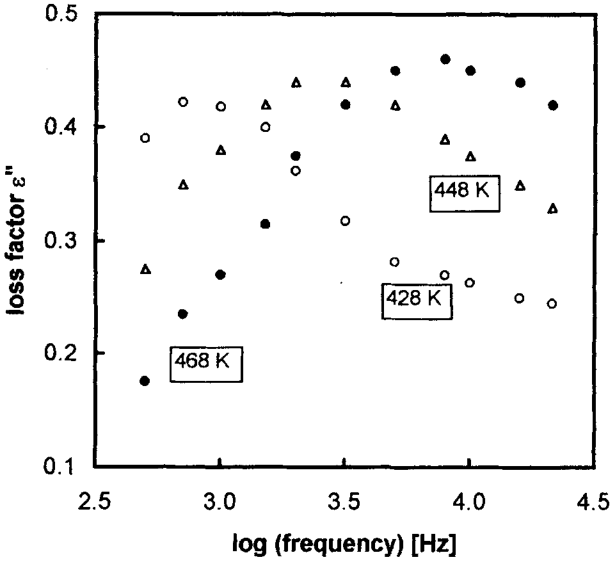

FIGURE 9 Spectral shape of the imaginary part of the complex permittivity of glass-bead-polystyrene composite for various temperatures. o 428 K, Δ 448 K, ● 468 K. The volume fraction of the filler was 12.5% Redrawn after [42].

Amorphous polymers containing crystalline inclusions may be an example of MWS relaxations in one-component systems. It has been shown that there is a link between the degree of crystallinity and the peak value of the loss factor due to MWS polarization in poly(ether-ether-ketone) [43], *i.e.* it is possible to estimate the crystallinity of such a system using BDS. MWS polarization phenomena may also be expected to occur in one-component systems dominated by hopping or percolation electrical transport. In such systems there may exist some regions characterized by comparatively easy jumps or transitions of charge carriers. These regions correspond to well-conducting inclusions in an insulating environment and may give rise to a remarkable dielectric dispersion. However, any quantitative conclusions in such cases are very difficult because the size, shape and spatial distribution of such "well-conducting" regions is usually subject to unknown stochastic distributions.

2.3. Adsorption of Solid Surfaces

A special case of a multiphase system is a system consisting of solid adsorbent and adsorbed surface layer. It may be shown that under conditions of dielectric additivity the effective relative permittivity is given by [9]:

$$\varepsilon'_{\mathrm{eff}} = \varepsilon'_1 + (\varepsilon'_2 - \varepsilon'_1) v_2 \tag{8}$$

where ε'_1 and ε'_2 are the relative permittivities of the adsorbent and adsorbed layer, respectively, and v_2 is the volume fraction of the adsorbed layer. The slope of the $\varepsilon_{\mathrm{eff}}(v_2)$ curve equals $\varepsilon'_2 - \varepsilon'_1$, so it is possible to find the permittivity of the adsorbed film, ε'_2, if the permittivity of the adsorbent, ε'_1, is known. This enables one to investigate the physical properties of thin adsorbed films as a function of their thickness, which is of importance for many branches of applied science. As an example, we can mention the investigations of adsorption of butane on silica gel [10] and the use of BDS for investigations of surfactants on solid surfaces useful for the pharmaceutical purposes [8]. It should be mentioned that dielectric measurements have shown that there is an essential difference between the properties of adsorbed polar and non-polar molecules. It turns out that the permittivity of the monolayer of polar molecules adsrobed on titanium oxide, glass and silicon is usually smaller than the value of the permittivity of the bulk liquid state, and the permittivity is very weakly dependent on temperature. It is suggested that both the reduced permittivity and its weak temperature sensitivity result from restricted reorientation of adsorbed molecules between a number of defined orientational positions [10].

Similar investigations might be useful for microelectronics where we often have to do with films thin enough for thickness-dependent phenomena to occur.

Adsorption of water on solid surfaces is a particularly important research problem. The BDS may be used as an effective research tool for investigations of this phenomenon. The changes of the dielectric properties due to the presence of adsorbed water molecules is very interesting for at least two reasons. The first one is that the materials may be used as moisture sensors and, secondly, dielectric measurements may enable one to define the mechanism of adsorption phenomena. A good example of searching for moisture sensors is the investigations presented by Sadaoka *et al.* [44]. They examined the permittivity of cellulose acetate and cellulose acetate butyrate (see Fig. 10) at a frequency 1 kHz. The cellulose acetate samples turn out to be more sensitive to the changing humidity but the samples of cellulose acetate butyrate show less hysteresis, hence the latter was suggested to be a suitable material as a sensor. The authors also tried to explain the molecular mechanism of adsorption of water molecules onto the cellulose samples. According to their suggestions, part of the water molecules are sorbed onto the cellulose polymers and the remainder forms clusters by hydrogen bonding. This second process is supposed to give rise to the hysteresis shown in Figure 10.

Let us mention two other examples of dielectric detection of water adsorption on solid surfaces. Matsuguchi *et al.* [45,46] examined poly(methyl methacrylate) films and acetylene-terminated polyimide resins searching (successfully) for materials with lesser hysteresis.

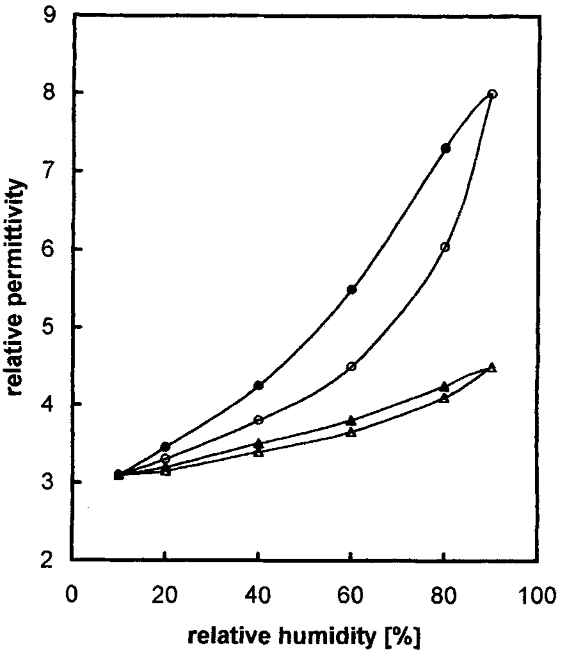

FIGURE 10 Permittivity as a function of relative humidity at 1 kHz. Cellulose acetate: o humidification, ● desiccation. Cellulose acetate butyrate: Δ humidification, ▲ desiccation. Redrawn after [44].

Shahidi *et al.* investigated the low frequency dielectric response of humid sand [47] which may be regarded as an example of an electrolyte system of lowered dimensionality. They found it possible to distinguish between the dielectric losses due to electrical conduction in the continuous paths through the system and the losses associated with the relaxation phenomena at the sand-water interface.

The examples of low frequency dielectric measurements presented above justify the conclusion that this measuring technique may be used for a very broad scope of research problems related to inhomogeneous systems.

3. CONCLUSIONS

Broadband Dielectric Spectroscopy may provide very important information about the physical properties of both one-component and multi-component inhomogeneous structures. In the case of multi-component composites the information refers both to the interactions between the composite components and to the physical properties of the additional phase, often called the interphase, originating between the surface of the basic components of the composite. In particular, BDS may be a very efficient research method for investigations of water-ageing of polymer composites. Broadband dielectric measurements make it possible to examine the influence of water as a modifier of aged polymer composites while the measurements of viscoelestic properties enable one to detect, *e.g.*, the influence of water as a plasticizer for the composite and for the matrix itself. In some cases, broadband dielectric measurements enable one to detect the changes of adhesion of the composite components resulting from water ageing.

Broadband dielectric measurements of adsorbing systems also enable one to investigate the physical properties of thin film adsorbed materials and their interaction with the adsorbent surface, which may be very useful from a practical point of view.

The application of high-frequency dielectric measurements to investigations of inhomogeneous systems is quite a different problem. High-frequency methods enable one to develop a very deep insight into the problem of quality of joints and absorption of water into composite materials. High-frequency dielectric investigations of epoxy resin joints of aircraft grade aluminium may be a good example at this point [48]. However, the high frequency methods are technically much more difficult and thus not so widely used as the low frequency dielectric measurements.

References

[1] Lipatov, Y. S., *Physical Chemistry of Filled Polymers* (in Russian) (Izdatelstvo Naukova Dumka, Kiev, 1967).

[2] Lipatov, Y. S., "Relaxation and Viscoelastic Properties of Heterogeneous Polymeric Compositions", *Advanc. Polym. Sci.* **22**, 1 (1977).

[3] Kryszewski, M. and Bąk, G. W., *Polish J. Chem.* **70**, 1 (1996).

[4] Boyd, J. C., Hakes, L. B., Purves, J. and Davies, C., *J. Pharm. Pharmacol.* **41**, 35 (1989).

[5] Craig, D. Q. M., Davies, C. F., Boyd, J. C. and Hakes, L. B., *J. Pharm. Pharmacol.* **43**, 444 (1991).

[6] Abe, M. and Ogino, K., *J. Coll. Inter. Sci.* **80**, 58 (1981).

[7] Craig, D. Q. M. and Macdonald, C., *J. Phys. Chem.* **99**, 5413 (1995).

[8] Craig, D. Q. M., *Dielectric Analysis of Pharmaceutical Systems* (Taylor and Francis, London, 1995).

[9] Hill, N. E., Vaughan, W. E., Price, A. H. and Davies, M., *Dielectric Properties and Molecular Behavior* (van Nostrand-Reinhold, London, 1969).

[10] McIntosh, R., *Dielectric Behavior of Physically Adsorbed Gases* (Arnhold, London, 1996).

[11] McGrum, N. G., Read, B. E. and Williams, G. W., *Anelastic and Dielectric Effects in Polymeric Solids* (Wiley, London, 1967).

[12] Blythe, A. R., *Electrical Properties of Polymers* (Cambridge Univ. Press, Cambridge, 1979).

[13] Hedvig, P., *Dielectric Spectroscopy of Polymers* (Adam Hilger Ltd., Bristol, 1977).

[14] Haran, E. N., Gingas, H. and Katz, D., *J. Appl. Polym. Sci.* **9**, 3505 (1965).

[15] Aliotta, F., Fontanella, M. E., Galli, G., Lanza, M., Migliardo, P. and Salvato, G., *J. Phys. Chem.* **97**, 733 (1993).

[16] Boudakian, B., Hill, R. M., Strivens, T. A. and Dissado, L. A., *Coll. Polym. Sci.* **269**, 938 (1991).

[17] Batra, A. K., Mathur, S. C. and Mansingh, A., *Phys. Stat. Sol.* (a) **77**, 399 (1983).

[18] Mitoff, S. P. and Charles, R. J., *J. Appl. Phys.* **43**, 927 (1972).

[19] Macdonald, J. R., *J. Chem. Phys.* **22**, 1317 (1954).

[20] Jonscher, A. K., *Phil. Mag. B* **38**, 587 (1978).

[21] Jonscher, A. K., *Dielectric Relaxation in Solids* (Chelsea Dielectric Press, London, 1983).

[22] Jonscher, A. K., *Universal Relaxation Law* (Chelsea Dielectric Press, London, 1996).

[23] Bąk, G. W., Szymański, A. and Jonscher, A. K., *J. Chem. Soc., Faraday Trans. 2* **81**, 1053 (1985).

[24] Bąk, G. W., *J. Mat. Sci.* **23**, 2365 (1988).

[25] Bąk, G. W., *J. Phys. C: Solid State Phys.* **21**, 3447 (1988).

[26] Bąk, G. W., *J. Phys.: Condens. Matter* **4**, 2557 (1987).

[27] Bąk, G. W. and Lipiński, A., *Thin Solid Films* **151**, 289 (1987).

[28] Bąk, G. W., *J. Phys. C: Solid State Phys.* **19**, 3173 (1986).

[29] Lipiński, A., Mycielski, W. and Świątek, J., *J. Phys. Chem. Solids* **41**, 455 (1980).

[30] *Two-phase polymer systems*, Utracki, L. A., Ed. (Hanser Publ. Munich, 1991).

[31] Strolbl, G., *The Physics of Polymers* (Springer-Verlag, Berlin, 1996).

[32] Steeman, P. A. M., Baetsen, J. F.H. and Maurer, F. H. J., *Polym. Eng. and Sci.* **32**, 351 (1992).

[33] Maurer, F. H. J., in *Controlled Interphases in Composite Materials*, H. ishida, Ed. (Elsevier, New York, 1990).

[34] Steeman, P. A. M. and Maurer, F. H. J., *Composite Interfaces* **1**, 1 (1993).

[35] Steeman, P. A. M., Maurer, F. H. J. and van Es, M. A., *Polymer* **32**, 523 (1991).

[36] Fripiat, J. J. and Jelli, A., *J. Phys. Chem.* **69**, 2185 (1965).

[37] Bastioli, C., Casciola, M. and Castelli, A., in *Interfaces in Polymer, Ceramics, and Metal Matrix Composites*, Ishida, H., Ed. (Elsevier, New York, 1988).

[38] Beek, van K. H., in *Progress in Dielectrics*, Birks, J. B., Ed. (Heywood, London, 1967), vol. 7, p. 69.

[39] Banhegyi, G., Rho, M. K., Chien, J. C. W. and Karasz, F. E., *J. Polym. Sci.* **B25**, 57 (1987).

[40] Tsangris, G. M., Psarras, G. C. and Kantopoulos, A. J., *J. Non-Cryst. Solids* **131–133**, 1164 (1991).

[41] Aldrich, P. D., McGee, R. L., Yalvac, S., Bonekamp, J. E. and Thurow, S. W., *J. Appl. Phys.* **62**, 4504 (1987).

[42] Perrier, G. and Bergeret, A., *J. Appl. Phys.* **77**, 2651(1995).

[43] Perrier, G., *Composite Interfaces* **4**, 111 (1996).

[44] Sadaoka, Y., Matsuguchi, M., Sakai, Y. and Takahashi, K., *J. Mat. Sci. Lett.* **7**, 121 (1988).

[45] Matsuguchi, M., Sadaoka, Y., Sakai, Y., Kuroiwa, T. and Ito, A., *J. Electrochem. Soc.* **138**, 1862 (1991).

[46] Matsuguchi, M., Sadaoka, Y., Nosaka, M., Sakai, Y., Kuroiwa, T. and Ito, A., *J. Electrochem. Soc.* **140**, 825 (1993).

[47] Shahidi, M., Hasted, J. B. and Jonscher, A. K., *Nature (London)* **258**, 595 (1975).

[48] Hayward, D., Affrosman, S., Pethrick, R. and Wilford, P., *Nondestr. Test. Eval.* **6**, 45 (1991).