Dielectrics Newsletter
Scientific newsletter for dielectric spectroscopy
Issue february 2005

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Relaxation of Librational Mode in Confined Liquid Crystal

introduction

Dielectric spectroscopy can be applied to investigate multiple aspects of the influence of confinement on dynamic properties of liquid crystals impregnating porous matrices. Applications of dielectric spectroscopy for investigations of confined liquid crystals [1-7] revealed new information on the changes in the molecular mobility as well as changes in the phase transition temperatures as a result of the influence of the confinement.

Alkylcyanobiphenyls such as 4-n-octyl-4’-cyanobiphenyl (8CB) are liquid crystals, which have been deeply investigated in the past and whose dielectric bulk properties have been quite clearly understood. Their molecules have a large dipole moment (~5 D) oriented along the molecular long axis, which significantly simplifies the understanding of the dielectric behaviour. In the nematic phase in a geometry in which the probing electric field E is parallel to the director the relaxation due to the restricted rotation of the molecules about their short axis is detected. The temperature dependence of the corresponding relaxation times obeys empirical Arrhenius equation.

For the geometry in which the electric field E is perpendicular to the director n, the relaxation due to librational motion of the molecules should be observed. This process has characteristic frequencies about 10 times higher than the relaxation due to the molecular rotation. The available information on dynamics of librational mode even for bulk liquid crystals, to our knowledge, is scarce, because in order to obtain an appropriate orientation of molecules with respect to probing electric field the sample should be placed into magnetic field. This is very difficult because the samples cells used for measurements at very high frequencies (hundreds of Megahertz) are large and do not fit between poles of conventional magnets providing magnetic field sufficient for required molecular orientation.

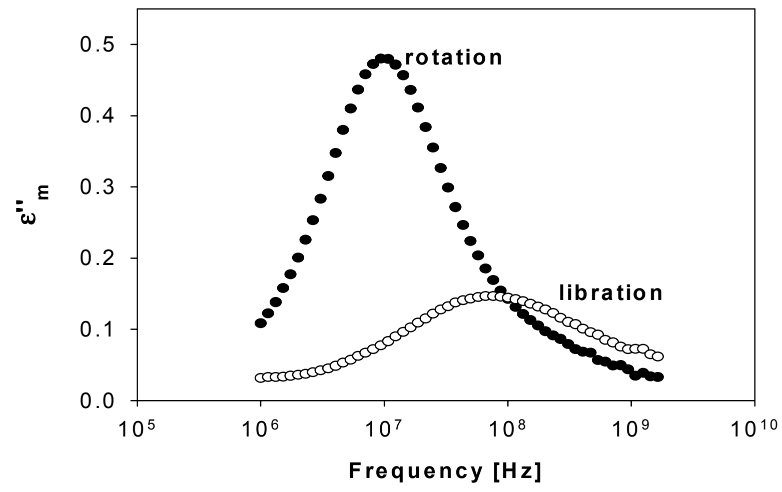

Fig. 1: Comparison of dielectric spectra of rotational (closed circles) and librational (opened circles) modes of 8CB confined in 200 nm cylindrical. All measurements taken at T = 310K.

liquid crystal confinement

To obtain quantitative description of the librational mode, we apply dielectric spectroscopy to investigate relaxation properties of 8CB confined in 200 nm cylindrical pores

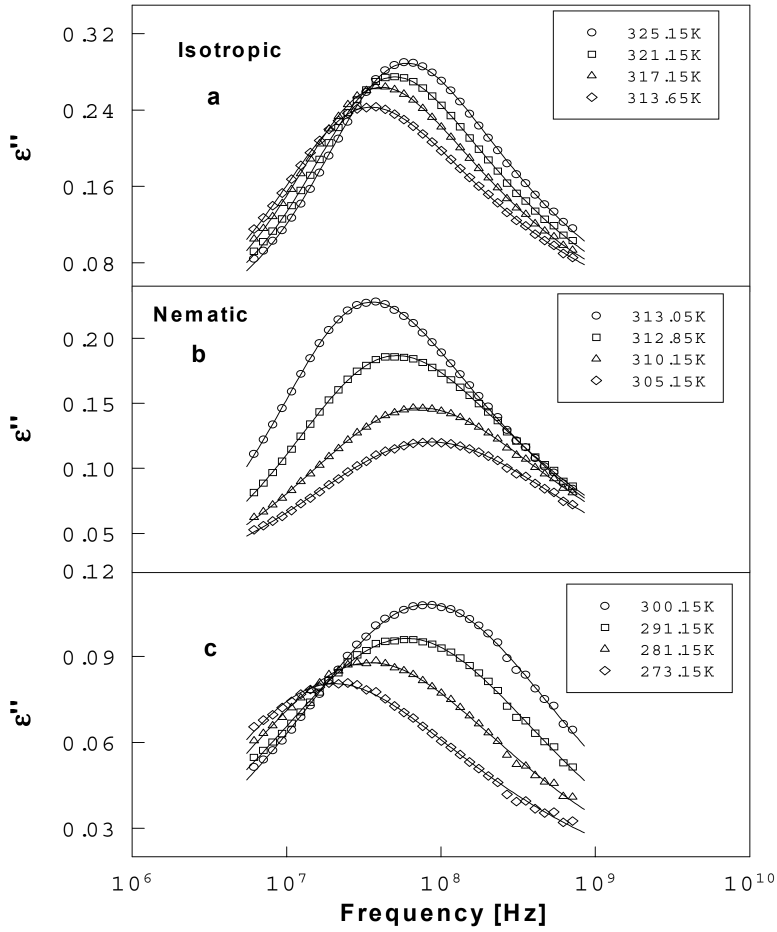

Fig. 2: Frequency dependence of the imaginary part of the dielectric permittivity of 8CB confined in 200 nm cylindrical lecithin treated pores (radial orientation of molecules) at different temperatures.

of Anopore membranes treated with lecithin. This treatment provides homeotropic boundary conditions (the molecules are oriented perpendicularly to the pore walls) for confined 8CB. Since the pore axis is parallel to the probing electric field and the molecular dipole moment is oriented perpendicularly to its direction, such a configuration makes it possible to investigate the dynamics of librational (tumbling) mode by dielectric method. In untreated pores the orientation of molecules is axial (the molecules are oriented in parallel to the pore axis) and the mode due to reorientation of molecules around short axis is detected. Therefore relaxations due to both mechanisms can be investigated separately in these pores. We used NOVOCONTROL equipment to perform these experiments.

relaxation processes

Figure 1 illustrates the difference in relaxation due to reorientation of molecules around short axis and due to their librational motion, observed in 8CB confined in cylindrical pores with axial (parallel to the probing electric field) and radial (perpendicular to the electric field) orientations. It is clear that the relaxation process in lecithin treated matrices (radial orientation) is observed at much higher frequencies than in the bulk sample and therefore, cannot be assigned to the same mechanism.

Since the molecules of 8CB do not have any component of dipole moment perpendicular to the long axis, the only explanation to the observed high frequency relaxation in the treated sample is to associate it with librational motion of molecules.

temperature dependence

The temperature dependence of dielectric spectra of the libration mode is complicated and very different from the behavior of the reorientation mode. Figure 2 shows three types of temperature dependences of the dielectric spectra observed for confined 8CB (with radial boundary conditions in anisotropic phases) in three ranges. In the temperature ranges corresponding to the bulk isotropic phase (a) and Sm-A and supercooled state (c), the positions of ε''_m move to lower frequencies with decreasing temperature.

The spectra for isotropic phase in this sample are due to the reorientation of molecules around their short axis, since there is no director in this phase and orientations of molecules in this phase are random. Therefore the temperature dependence of these spectra as well as the temperature dependence of the corresponding relaxation times - isotropic phase are typical for the isotropic phase of liquid crystals. In nematic phase (Fig. 2, b), the positions of ε''_m move to higher frequencies with decreasing temperature, indicating the faster relaxation rate at lower temperatures.

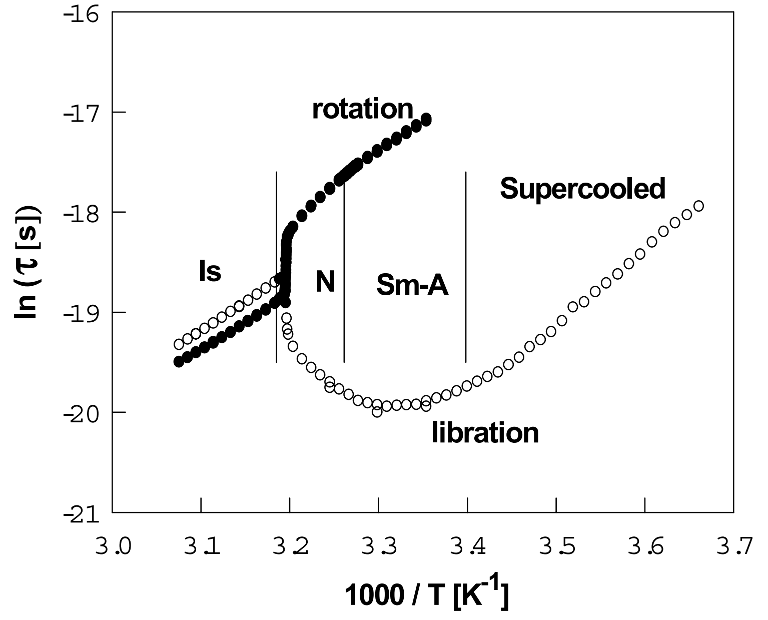

Fig. 3: Temperature dependences of relaxation times of the processes due to reorientation of molecules around their short axis (closed circles) and of relaxation times of the librational mode (opened circles) in confined 8CB. In isotropic phase the relaxation times correspond to the process due to the rotation of molecules around their short axis for both graphs.

relaxation times of rotation and libration processes

The temperature dependence of the relaxation times (libration mode) obtained for 8CB confined in lecithin treated cylindrical pores is illustrated in Fig. 3.

The temperature dependence of relaxation times of this mode is totally different from the behaviour observed in investigations of relaxation due to reorientation of molecules around their short axis (see Fig 3). The relaxation time of librational mode in the temperature range corresponding to the nematic phase increases upon increasing the temperature towards the nematic-isotropic transition temperature. In contrast, the temperature dependence of the relaxation times of the process due to reorientation of molecules around the short axis decreases upon increasing the temperature in the same temperature range. The interpretation of the results obtained in nematic phase needs the involvement of the temperature dependence of the orientational order parameter. The decrease of relaxation time in the temperature range corresponding to the nematic phase of 8CB could be due to an acceleration of the process with increasing the order parameter.

In the sample with homeotropic (radial) boundary conditions, in the case of perfect order and taking into account that the dipole moment of the molecule is parallel to its long axis, the projection of the dipole moment on the direction of the electric field, which is along the pore axis, is minimal because the fluctuations of the molecular orientations with respect to the radial direction are very small. These fluctuations of the dipole moment (or molecular long axis) correspond to the librational motion of the molecule and the amplitude of the fluctuations determines the relaxation rate of the dipole in the viscous media. At higher temperatures, these deviations (fluctuations) are of greater amplitude (the order parameter is smaller) and this requires longer time to complete one librational cycle. As a result, the relaxation rate is smaller for fluctuations of greater amplitude and vice versa. Such behaviour has resulted in the particular temperature dependence of relaxation times observed for the librational mode in the nematic phase temperature range. In the smectic-A phase and supercooled state, the temperature dependence of relaxation times is mainly determined by the variations of viscosity.

The dynamics of the librational mode is totally different from the behaviour observed in investigations of relaxation due to reorientation of molecules around their short axis.

The interpretation of the temperature dependence of relaxation time needs the involvement of the temperature dependence of orientational order parameter and suggests that the better orientational order the faster the process due to libration of molecules.

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Amine Cured Epoxy Layers on Metals – Network Dynamics During Thermal and Hygrothermal Ageing

introduction

The broad application of adhesive joints and polymer layers in engineering is always coupled with the topic of durability. Understanding of the fundamental ageing mechanisms and their influence on adhesion and molecular structure in polymer metal bonds is essential for the improvement of durability.

Due to its sensitivity to rotations of permanent dipoles in the electric field, dielectric spectroscopy (DES) offers the possibility to characterise molecular dynamics in polymers over a large frequency range.

In this paper the changes of network dynamics are reported for an amine-cured epoxy adhesive on metals during thermal and hygrothermal ageing. The modification of macromolecular dynamics is studied by DES over a period of 100 days of exposure.

experimental details

The metal substrates are prepared by physical vapour deposition of pure Al or Cu on silicon wafers. The resulting metal surfaces are covered by their native oxides and by the usual adsorption layer from ambient carbonaceous contaminants. The adhesive regarded in this paper consists of diglycidylether of bisphenol A (DGEBA) as the epoxy resin and diethylene triamine (DETA) as the curing agent (100 : 14 by weight).

Resin and hardener are thoroughly mixed in the molten state at 55 °C (melting point of DGEBA: 42 °C) for 5 min in a closed glass vessel. During rapid cooling down to room temperature within about 1 min, further stirring is performed.

Epoxy layers of 5 µm or 25 µm thickness (d_{EP}) are prepared by casting the reactive mixture on the substrates. Curing proceeds at room temperature for 48 h followed by a 1 h post-curing step at 120 °C in dry, CO_2-reduced atmosphere (dew point: -70 °C, CO_2 content: < 200 ppm). Then, the samples are stored at 40 °C either in argon or in regular moist air (90 % r.h.) for up to 100 d. At selected ageing times, samples were taken from the ageing vessel, dried in vacuum and evaporated with an Al counter electrode (∅ = 5 mm). The modification of their macromolecular dynamics was studied by dielectric broadband measurements in a frequency range of 10^{-2} Hz to 10^{6} Hz carried out with a NOVOCONTROL High Resolution Dielectric Alpha Analyser.

In the first step, the ageing effects on the local dynamics (sub-T_g-relaxation) in the epoxy layers were analysed by isothermal frequency scans in the range from -80 °C to +40 °C (ΔT = 5 K) – see Fig. 1 for an example. Afterwards, the

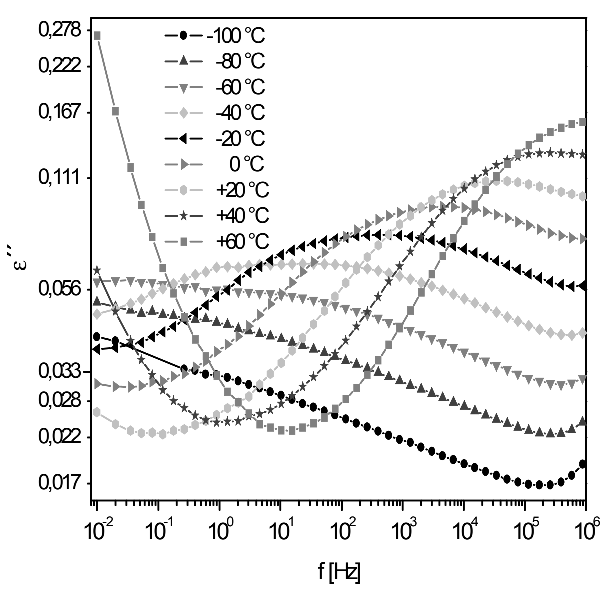

Fig. 1: Dielectric loss spectra ε″(f, T) for a 25 µm epoxy on Al prior to ageing. Only the secondary relaxation process is present. For T > 30 °C the high frequency wing of the α-relaxation appears.

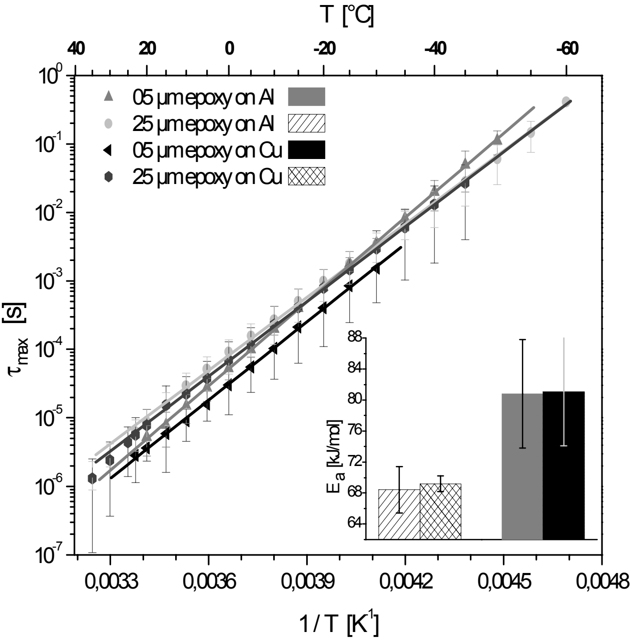

Fig. 2: Arrhenius plot –log τ vs. 1/T for epoxy layers on metals prior to ageing. In the inset the activation energy E_a, given by the linear fits, demonstrate the increased activation energies in the 5 µm epoxy layers.

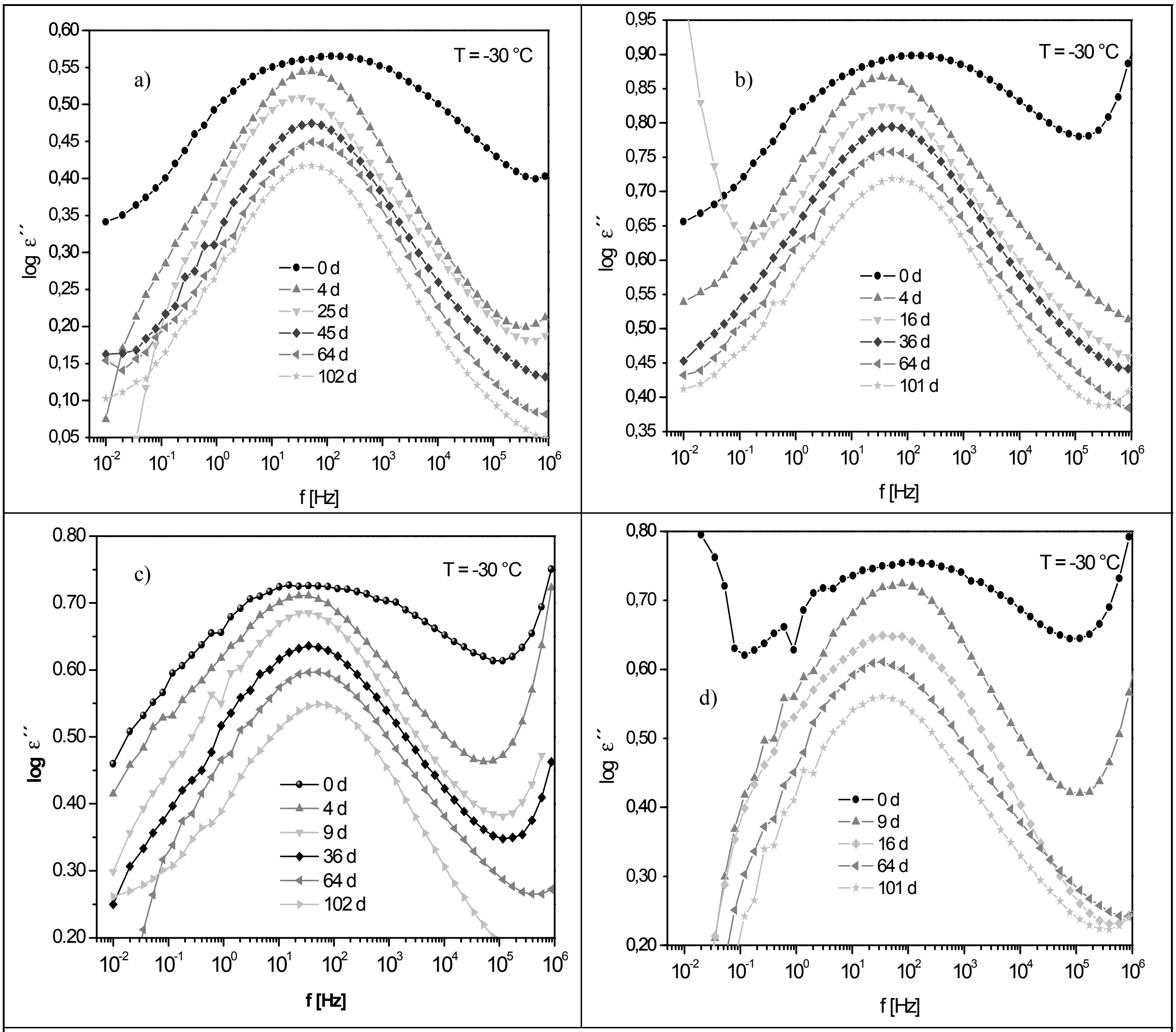

Fig. 3: Dielectric loss spectra ε''(f) during hygrothermal ageing at T = –30 °C of a
a) 25 µm epoxy on Al, b) 25 µm epoxy on Cu, c) 5 µm epoxy on Al and d) 5 µm epoxy on Cu.

influence of ageing on the glass transition (α-relaxation) was investigated by experiments at fixed frequencies and continuously increasing temperature (from -10 °C to +200 °C, with β = 8 K/min).

results and discussion

In the glassy state, the dielectric properties of the epoxy layers are dominated by the local motions of molecular dipoles in the network (cf. the peaks in Fig. 1). A decrease of temperature results in a more and more constrained network dynamics which reduces the local motions. A measure for the energy to activate these processes is given by the apparent activation energy E_a given by the Arrhenius equation which describes the relaxation time of the secondary relaxation as a function of temperature: $\tau^{\beta}_{\max} = \tau^{\beta}_{\infty} \exp\left[\frac{E_a}{RT}\right]$.

The Relaxation time $\tau_{\max} = 1/2\pi f_{\max}$ for the maximum $f_{\max}$ of the secondary relaxation peak in ε''(f) is obtained by fitting by a Havriliak-Negami function [1,2].

The Arrhenius plot (Fig. 2) provides straight lines for $\tau_{\max}(1/T)$ thus classifying the observed process as a secondary relaxation. Prior to ageing, the local dynamics are characterised by increased activation energies in the 5 µm epoxy layers as compared to the 25 µm layers (inset of Fig. 2). For both d_{EP}-values, the mean activation energies on Cu tend to be somewhat higher than on Al. Thus, the local dynamics of the non-aged state depends on epoxy thickness and slightly on substrate material.

During ***hygrothermal ageing***, two significant changes are observed in the spectra of the epoxy layers (cf. $\varepsilon''(\omega)|_{T=-30\,°C}$ in Fig. 3 as example). During the first four days, the secondary relaxation peak reduces its width which corresponds to a narrowing of the relaxation time distribution for the local mobility. This effect is obvious on both substrates for both d_{EP}-values.

In the course of further ageing, the relaxation peak shifts in position. For all 25 µm layers and for the 5 µm layers on Al, the relaxation peak shifts to higher frequencies whereas the peak in the 5 µm layers on Cu tends to shift to lower frequencies.

During ***thermal ageing*** (e.g. Fig. 4), the width of the relaxation time distribution also reduces significantly within the first four days. But in the further course of ageing the relaxation peak is stable in position and width in contrast to hygrothermal ageing.

Accordingly, both thermal and hygrothermal ageing reduce the width of relaxation time distributions within the first days. In addition, hygrothermal ageing affects the average local network dynamics. The changes are specific for the substrate material and depend on the layer thickness d_{EP}.

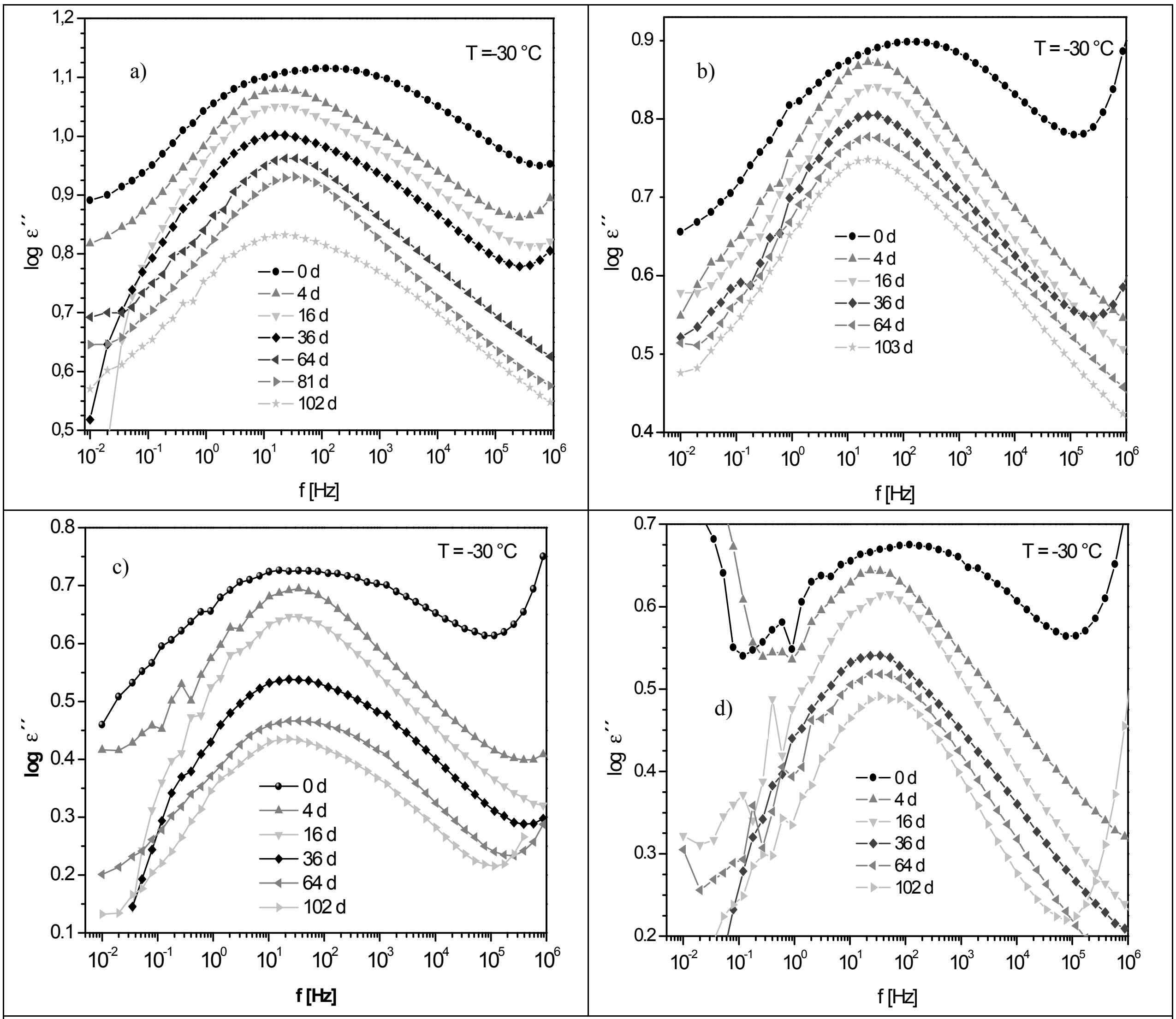

Fig. 4: Dielectric loss spectra ε''(f) during thermal ageing at T = –30 °C of a
a) 25 µm epoxy on Al, b) 25 µm epoxy on Cu, c) 5 µm epoxy on Al and d) 5 µm epoxy on Cu.

The cooperative macromolecular mobility of the α-relaxation in the epoxy layers is considered by dielectric measurements with a constant heating rate β at a number of fixed frequencies. For the non-aged state, these temperature scans show the dynamic glass transition for the epoxy matrix in the range of 130 °C – 160 °C at 100 Hz (see Fig. 5). As indicated by the strong increase of the permittivity ε' above

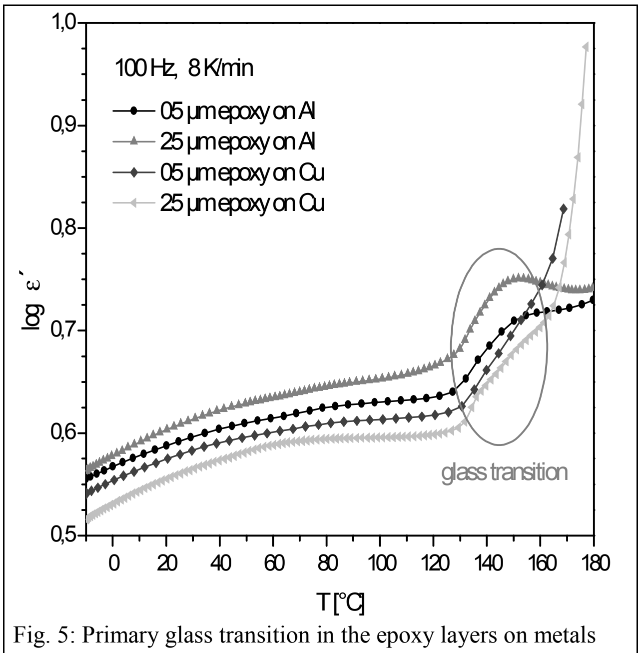

Fig. 5: Primary glass transition in the epoxy layers on metals prior to aging.

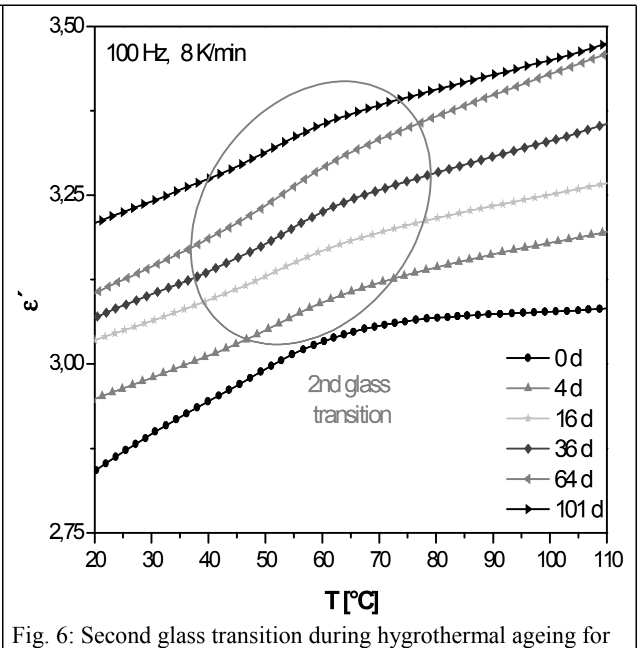

Fig. 6: Second glass transition during hygrothermal ageing for 25 µm epoxy on Cu.

+150 °C, the epoxy layers on copper are stronger affected by electrode polarisation. During hygrothermal and thermal ageing as well, a second glass transition $T_{g,2}$ emerges within four days of ageing, well below the matrix glass transition (see Fig. 6 for example).

It indicates that a new, more mobile phase separated inside the epoxy matrix.

The effects of ongoing ageing on the two glass transitions are quite complex. During the 100 days of ***hygrothermal ageing***, the T_g of the matrix glass transition goes through a maximum (see Fig. 7) which is more obvious on Cu than on Al. Moreover, the maximum on Cu is more pronounced for the thinner epoxy layers. For the 25 µm epoxy on Al, the T_g increases almost monotonously. All that indicates a superposition of several processes induced by ageing.

During ***thermal ageing*** (Fig. 8) only the T_g of the 5 µm epoxy layers on Al tends to rise by 4 K. T_g of the other samples seems to be not affected by thermal ageing over a period of 100 days.

The behaviour of $T_{g,2}$ is very specific for the two d_{EP}-values and for the metal substrates (Fig. 9). For the 5 µm layers on Al and Cu, $T_{g,2}$ increases with different rate by ~3 K during hygrothermal ageing. In the 25 µm layers, $T_{g,2}$ is not clearly affected on Cu whereas $T_{g,2}$ goes through a maximum on Al and decreases to a value 4 K below the initial $T_{g,2}$.

In contrast, thermal ageing stimulates a remarkable increase of $T_{g,2}$ in all epoxy layers (Fig. 10). The effect is more pronounced in the 5 µm layers.

conclusion

Thermal and hygrothermal ageing over 100 days lead to obvious changes of the network dynamics in the epoxy layers studied in this work. These changes result from modifications of the epoxy that are not only specific for the ageing conditions but also depend on the substrate material. Furthermore, these aging effects are more intense in thinner epoxy layers. Surprisingly, the substrate affects the epoxy over such great distances as 5 µm.

The chosen ageing conditions are relatively mild and proceed in the glassy state of the epoxy. Nevertheless, they produce a new glass transition well below the primary glass transition of the epoxy matrix. This indicates the separation of a second phase with increased cooperative mobility. Both glass transitions are affected in specific ways by ageing.

Further investigations are in progress in order to understand which mechanisms are activated during ageing and how they affect the chemical structure and the morphology of the epoxy layers.

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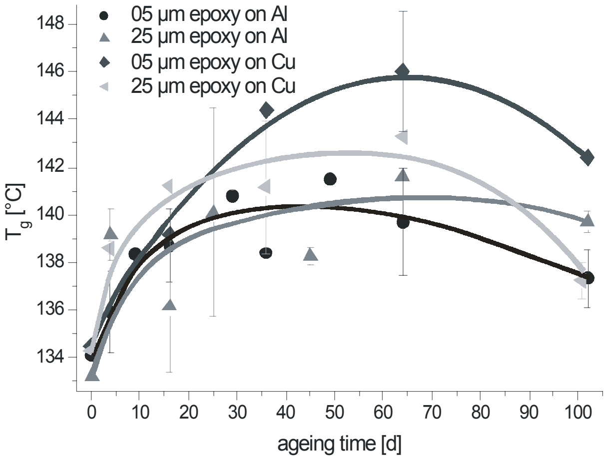

Fig. 7: Matrix glass transition T_g during hygrothermal ageing for epoxy layers on metals.

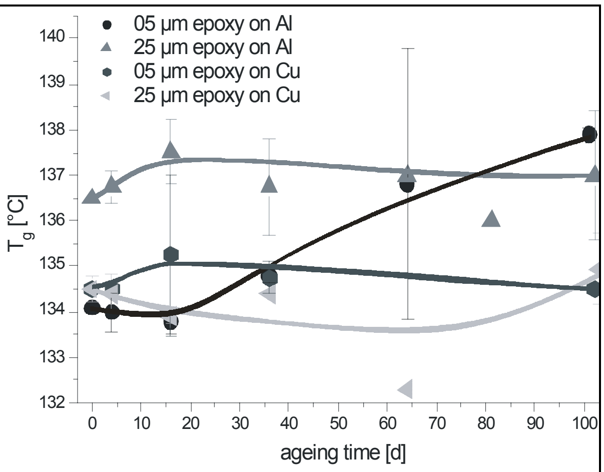

Fig. 8: Matrix glass transition T_g during thermal ageing for epoxy layers on metals.

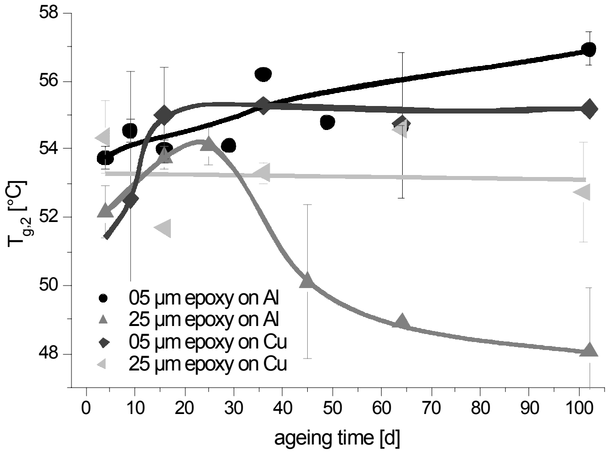

Fig. 9: Second glass transition $T_{g,2}$ during hygrothermal ageing for epoxy layers on metals.

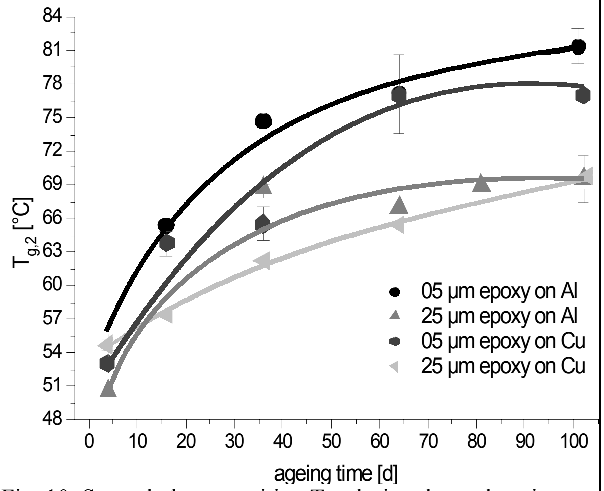

Fig. 10: Second glass transition $T_{g,2}$ during thermal ageing for epoxy layers on metals.

Graham Williams

Broadband Dielectric Spectroscopy and its Application 2004 in Delft

The 3rd International Conference on Dielectric Spectroscopy and its Applications was held at Delft University of Technology on 23-26 August 2004. Organised by Prof. Michael Wübbenhorst and his team at the TU-Delft, the conference followed the tradition of earlier DRP Meetings held at Jerusalem and Leipzig.

It was attended by over 160 scientists from 30 countries; 65 lectures were given and 105 Posters presented, describing current researches using broadband dielectric spectroscopy (BDS). The large attendance included a high proportion of young scientists. New researches and active discussions between participants demonstrated the welcome resurgence internationally of dielectrics science.

The Meeting was supported financially by the TU Delft, DCM-TU Delft, KNAW, FOM and DSM in the Netherlands and Novocontrol Technologies.

The variety of topics in the invited talks was exceptional, ranging from the very fundamental (e.g. Kramers-Kronig relations by van Turnhout) to applications of BDS to complex systems (e.g. of treated blood serum by Gorobchenko et al).

As in the previous Conferences many presentations described the structural and secondary relaxations in amorphous polymers and glass-forming liquids, as measured over large frequency/temperature ranges (Böhmer, Frick, Richert, Nozaki, Alegria, Yagihara, Capaccioli, Massalska-Arodz, Vassilikou-Dova, Stevenson) together with studies of pressure/temperature effects (Roland, Casalini, Floudas). Theoretical models were proposed for multiple processes in amorphous systems (Diezemann, Dyre, Halpern, Eker).

BDS studies were described for polymer blends/mixtures (Ngai), liquid mixtures (Blochowicz), water-containing systems (Feldman, Lyashchenko, Swenson, Vassilikou-Dova, Devautour-Vinot, Grineva, Grigera, Hernandez-Perni, Caduff), biological systems (Gatash, Stapert, Sekine), ferroelectric materials (Furukawa, Gerhard-Multhaupt, Bauer, Pawlaczyk, Fichtl, Ben Ishai), liquid crystals (Kresse, Sinha, Aliev, Dantras) and nano/meso-structures (Stevens) together with real-time BDS studies of crystallization (Ezquerra, Wurm), bulk polymerization (Johari) and physical aging (Fukao, Wypych). AC ion-conductivity studies of solids were also described (Leon, Runt, Kranbuehl, McLachlan). A tribute to the late Prof. Dan Kivelson was given by the writer.

Newer topics included nanoscale and non-linear conductivity spectroscopy in inorganic solids (Roling), BDS studies of molecular dynamics in ultra-thin layers and in confined environments (Kremer, Wübbenhorst, Fukao, Schönhals, Serghei), molecular dynamics simulations of isotropic and oriented polystyrene (Lyulin), non-resonant hole-burning of glass-forming liquids (Blochowicz) and non-linear dielectric resonance spectroscopy of new cellular (foamed) ferroelectret polymers (Bauer, Gerhard-Multhaupt).

The large number of posters complemented the above talks, especially BDS studies of nano-confined films, of amorphous polymers, functional organic and inorganic materials (eg ferroelectrics), biological systems (blood serum, frog-muscle, bone collagen), conduction phenomena in organic polymers and inorganic solids, while new techniques were introduced (dielectric depth-profiling in epoxy coatings, temperature-modulated dielectric analysis for cure-monitoring).

In the Measurement Forum Dr Schaumburg gave a presentation of the NOVOCONTROL range of equipment.

Few talks and posters were concerned with the theory of dielectric relaxation and conduction of simple and complex materials.

This appears to be one area that needs more input to aid our understandings of the dielectric phenomena presented at this Meeting.

On the Tuesday evening Conferees enjoyed a Boat Excursion (with band and dancing) around the port of Rotterdam, during which the Conference Dinner was served, while on the Wednesday evening they were treated to superb solo performances by Profs. Kremer, Wübbenhorst and Gerhard-Multhaupt at a special Chamber Concert Scientists for Scientists held at the TU Muziekcentrum.

The organisation of BDS 2004 was excellent in every way. We thank Prof. Wübbenhorst and his team (PJ Droppert, VR Lupascu, P van Mourik, J van Turnhout and T Verheul-Mentink) for all they did before and during the Meeting to make this such a successful and memorable Meeting in the beautiful old city of Delft.

Further details can be seen at http://www.polymers.tudelft.nl/ids2004/index.html

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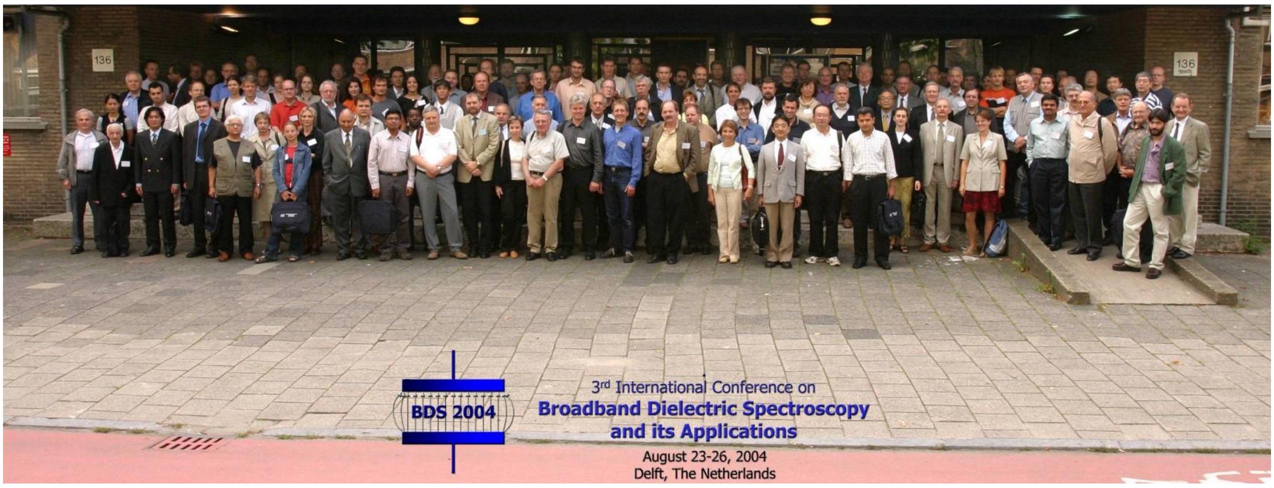
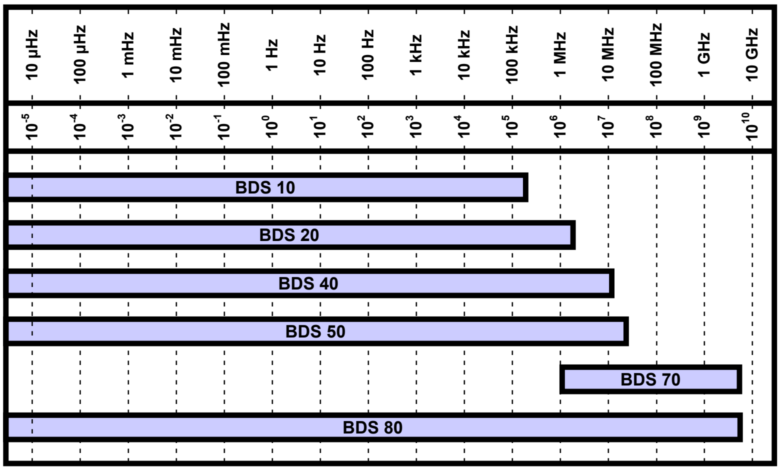


OVERVIEW

BROADBAND DIELECTRIC AND IMPEDANCE SPECTROSCOPY over 16 decades by Novocontrol Technologies



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