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COHERENT VIBRATIONS IN ‘POLAR/NON-POLAR’-LIKE COMPLEX POLYMERIC MIXTURES
A dielectric approach to percolation phenomena[*]

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Abstract

The analysis of thermostimulated currents by the fractional polarization procedure has been used to establish the existence of a coherent vibration in ‘Linseed oil/mastic varnish’ mixtures. This excitation is seen in the oil component when its proportion in the system is inferior to its percolation threshold. The observed phenomenon complies with compensation laws and is interpreted in the framework of the formalism developed by Fröhlich to understand collective phenomena in biological systems.

Keywords: coherent vibration, percolation, thermostimulated currents

Introduction

‘Macroscopic systems which exhibit an organized dynamic behaviour are frequently governed by a few collective degrees of freedom which dominate the rest. Such behaviour finds its expression in the existence of macroscopic wavefunctions which impose a long range coherence’. This idea [1] has been used as a working hypothesis by Fröhlich to understand collective phenomena in biological systems [1–4]. Nevertheless, to our knowledge, the actual physical vibrations have not yet been demonstrated by dielectric methods. This paper aims at presenting experimental evidence for such a coherent excitation in natural polymeric mixtures, made of linseed oil and mastic varnish, which approximate in their chemical complexity to biological systems. Their observation was made possible through the analysis of thermostimulated currents (TSC). The results obtained were used to understand percolation phenomena in these materials.

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Samples and experimental techniques

Linseed oil consists of a mixture of triglycerides with a range of saturated and unsaturated long chain fatty acids [5] up to C_{18}. The mastic varnish used in this study is a mixture of the natural resin mastic triterpenoid [5] (C30) and oil of turpentine solvent [5] (C10) in the ratio of 1:5(v/v). Three fresh mixtures were prepared with these starting materials adding lead based drier to linseed oil in the volume proportion of 1:8. They correspond to the volumetric proportions of varnish of 33.3, 50, 66.6% and are respectively labelled as mixtures 1, 2 and 3.

The principles of thermostimulated currents have been reported elsewhere [6–8]. By applying the ‘fractional polarization procedure’ the complex global relaxation modes are resolved into elementary Debye-like relaxation processes (fine structure), each following the Arrhenius equation:

$$\tau(T) = \tau_o \exp[\Delta H/kT]$$

where τ_o is a pre-exponential factor, k the Boltzman constant and ΔH the activation energy which is an increasing function of the size of the corresponding relaxation units [9]. When $\log\tau_o$ is a linear function of ΔH a compensation phenomenon is said to be observed and the relaxation times are given by the compensation law [10]:

$$\tau(T) = \tau_c \exp[\Delta H/k(T^{-1} - T_c^{-1})]$$

where T_c is the compensation temperature and corresponds to the slope of the above cited linear evolution. At T_c all the processes have the same relaxation time τ_c.

The samples were all analyzed within a parallel plate capacitor whose electrodes are 5 mm in diameter, with a separation of 1 mm between them. For ‘global’ measurements a 100 V mm^{-1} polarizing electric field E_p was applied at T_p=0°C and the depolarization current was recorded as a function of the temperature in the range of –100 to 25°C at a heating rate of 7°C min^{-1}. For each material the analysis was performed by using two different samples. These were measured consecutively under the same experimental conditions in order to check both the reproducibility of the sample preparation and of the measurements. The fine structures were obtained under the same experimental conditions with a starting temperature of –90°C, a polarization window of 10°C and a displacement step of 5°C for the polarizing temperature.

Experimental results and discussion

The global relaxation curves obtained with the oil and the resin components are shown in Fig. 1. Both are characterized by high temperature depolarization currents, either positive or negative, depending on the measurements. The latter ones are attributed to direct conductivity due to spontaneous charged-particles displacements between the electrodes [11]. Their substraction allowed all the relaxation processes to be resolved. They appear to be strictly confined within the temperature range of –100 to –15°C. Two structures are observed with the varnish component at –80 and –40°C; and three with the oil component at –82, –65 and –25°C.

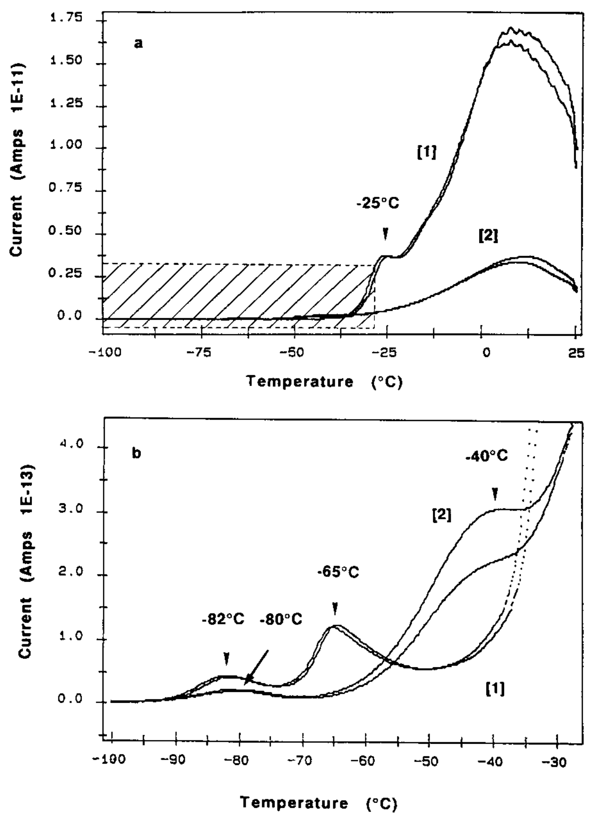

Fig. 1 Overall view (a) of the global relaxation curves in the drying oil [1] and the varnish [2]. In each case the measurements are performed with two different samples on the same material. The signal in the box is enlarged (b)

As the relaxation area found for the oil is at least one order of magnitude greater than that of the mastic varnish the signal in mixture 1, 2 and 3 is mainly due to the former material.

The global relaxation curves of mixture 2 obtained with different values of E_p, applied at T_p=0°C, are given in Fig. 2. The evolution of the relaxation area as a function of E_p is linear which establishes the dipolar character of the relaxation in this material [12, 13]. By analogy this character is attributed to every relaxation structure observed with the two starting materials and their mixtures.

The fine structure of mixture 2 is reported in Fig. 3. The compensation diagrams $\log\tau_0$ *vs.* ΔH is depicted for all the relevant materials in Fig. 4.

The two compensation laws observed with the varnish component are representative of cooperative phenomena due to hierarchically correlated motions: as the compensation temperature of the high temperature relaxation processes, i.e. [–100; –60°C] (labelled as 'resin 2' in Fig. 4) corresponds to the melting temperature of the resin mastic, namely 80°C, the latter are interpreted as precursors to the melting of the resin component in the mixtures. Due to the corresponding large increase in the

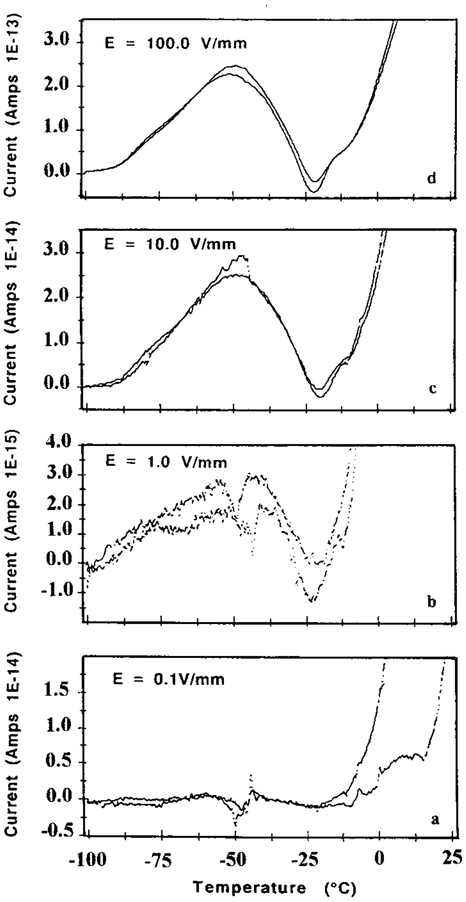

Fig. 2 Relaxation curves of mixture 2 obtained with different values E_{p}= 0.1 (a), 1 (b), 10 (c) and 100 V mm^{-1} (d) of the polarizing electric field applied at T_{p}=0°C

activation energy, the low temperature relaxation process, i.e. [–60; –20°C] (labelled as ‘resin 1’ in Fig. 4) is interpreted as the building up of an ordered phase in the resin component. Both relaxation processes correspond to inducive-type mechanisms where the term ‘inducive’ is to be understood in the sense that the motion of a small dipolar entity drives directly that of a larger one [14].

The fine structure of the oil is not accessible. It is suggested that it comes from the highly polar character of the long chain fatty acids. This generates a strong electrostatic interaction between the triglycerides and prevents the consideration of the relaxation of any elementary dipolar unit as a whole, i.e. without considering its neighbours: the fractional polarization procedure which constitutes already by itself a Debye approach is not relevant.

In mixture 1 a sufficiently large proportion of varnish (this material may be seen as an insulator with respect to the oil) has been introduced so that the strong electrostatic interaction between the triglyceride should be destroyed. The oil component

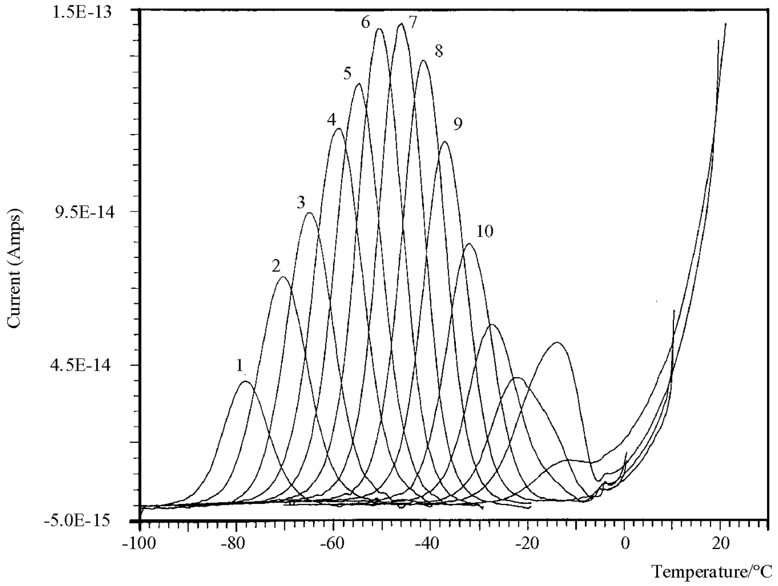

Fig. 3 Fine relaxation structure of mixture 2. Compensation peaks are numbered from 1 to 10

appears as a finite set of quasi-independent elementary relaxation units in which case a fine structure is accessible. In this mixture no compensation phenomenon is observed; the activation energy is independent of the temperature, having an average value of 1.17 eV. This leads to two conclusions: first the oil component in mixture 1 is indescribable in terms of clusters which means that its proportion in this material is superior to its percolation threshold [15–17]. Secondly the elementary relaxation processes in the oil are intrinsically of a non-cooperative nature; whatever the temperature is, they involve the same elementary dipolar unit.

In mixtures 2 and 3 five essential points characterize the relaxation processes in the oil component: (i) they follow compensation laws; (ii) these are superimposable and (iii) parallel to the one which governs the high temperature relaxation processes in the varnish; (iv) the first compensation peak of each fine structure corresponds to the same activation energy, i.e. 1.0 eV, which equals with the resin component in the varnish at the same temperature, namely –80°C; (v) the energy domain associated with the compensation phenomena extends as the proportion of oil increases.

Points (i) and (ii) indicate that the relaxation of the oil in mixtures 2 and 3 deals with the same kind of dipolar entities. Points (iv) and (v) establish that the maximum size of these entities increases with the proportion of oil in the mixtures. The definition of such dipolar entities as clusters constitutes a satisfactory representation of the systems.

The relaxation processes observed in the oil and the varnish are different. They are cooperative in the varnish and may thus be expressed in terms of giant dipolar oscillations or depolarization waves whose wavevector q is close to zero. Those ob-

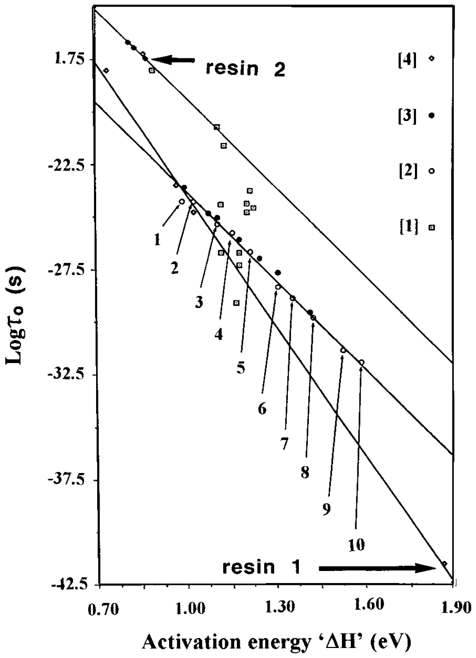

Fig. 4 Compensation diagrams for mixtures 1 [1], 2 [2] and 3 [3] and the mastic component [4]. Concerning the latter the low and high temperature relaxation processes are respectively labelled as 'resin 1' and 'resin 2'. Numbers 1 to 10 refer to the corresponding elementary relaxation peaks in the fine structure of mixture 2

served in the oil when the latter material forms a spatial continuum (refer to mixture 1) have a correlation length limited to the size of the relaxation units corresponding to an activation energy of 1.17 eV approximately. Wavevectors associated with such depolarization waves are finite and large.

Fröhlich makes the assumption that the state of thermal equilibrium in a system composed of non-interacting polarization waves with frequencies in a narrow range and which is placed into a heat bath at a given temperature T exhibits a Böse condensation over the q=0 polarization wave with the lower frequency [1, 2]. In mixtures 2 and 3 this effect forces the depolarization wave in any oil cluster to be in phase with that of the resin component. This leads to the excitation of a coherent vibration in these systems. It finds its expression in the fact that the compensation temperature associated with the oil relaxation processes corresponds to the melting temperature of the resin component (refer to point (iii)).

Point (iv) indicates that the relaxation of the smallest oil clusters is initiated at about –80°C by the relaxation of an ordered phase of the resin component whose critical size corresponds to an activation energy of 1 eV. In practice it is suggested that the q=0 depolarization wave is forced in all the oil clusters at the same temperature: the equivalent propagation of this depolarization wave inside the relaxation units (oil clusters), regardless of their size, justifies the existence of cooperative effects in the oil, which are demonstrated by the adherence to compensation laws (refer to point (i)). These compensation phenomena are unusual in the sense that they do not depend on 'inducive-type' relaxation processes [18, 19].

Conclusions

This paper presents experimental evidence for the existence of a coherent vibration in 'linseed oil-mastic varnish' mixtures where the proportion of oil is inferior to its percolation threshold. The observed phenomenon complies with compensation laws which do not depend on 'inducive-type' relaxation processes. Furthermore, the results demonstrate the suitability of the TSC technique for the study of percolation phenomena in complex polymeric mixtures. Further work is in progress to investigate in more detail the percolation region of linseed oil in these systems by dielectric spectroscopy.

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