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Thermally-stimulated creep spectroscopy in the study of physicochemical ageing of LDPE [1]

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Abstract

In polymeric power cables, the physicochemical ageing of the insulator is an important limiting factor of its lifetime. The present work reports a comparative study performed on additive-free low-density polyethylene (LDPE) aged in different electrolytes under an electric field. The influence of the electric field, ageing temperature and ionic species on LDPE was investigated by thermally stimulated creep (TSCr) spectroscopy.

The TSCr spectrum of reference LDPE shows the existence of three mechanical retardation modes, labelled α, β and γ in order of decreasing temperature. The α-mode has been associated with mechanisms involving the rigid amorphous domains stressed by crystallites, while the β- and γ-modes have been attributed to the amorphous phase. The experimental data deduced from the analysis of TSCr spectra have been plotted on a compensation diagram: they define the "structure" of the disordered phases of reference LDPE.

The comparative study of various aged LDPE samples shows that the para-crystalline phase or the rigid amorphous phase is affected first. In a second step, ageing mechanisms hinder the relaxational process of the amorphous phases and the material becomes fragile and brittle at a rate that is a function of the ionic solution used.

INTRODUCTION

Insulating polymeric materials (polyethylene, polypropylene) are generally semi-crystalline. They are constituted by an intimate mixture of ordered crystals (lamellar crystallites and/or spherulites) and a metastable randomly structured amorphous region. There is an interphase between these two phases: para-crystalline domains and/or rigid amorphous domains stressed by crystallites.

With metastability of the amorphous phases, the properties of polymeric materials change with time if the temperature is lower than the glass transition. This spontaneous ageing is characterized by an endothermic phenomenon in differential scanning calorimetry [1].

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The physical ageing or structural recovery must be distinguished from the stimulated ageing caused by modifications of physical and/or chemical bonds caused, for instance, by electric stress or environmental conditions (water, ions, etc). These modifications affect fundamentally the molecular mobility of the disordered phases (para-crystalline domains, rigid amorphous domains and free amorphous phase).

The process by which the molecules rearrange is characteristic of the structure and the morphology of the polymer and proceeds at a rate which increases with temperature. The parameters defined to describe such a behaviour must therefore depend on time or frequency and temperature.

A quantitative study by thermally stimulated creep (TSCr) spectroscopy of its kinetics can be used to quantify the ageing procedure. In TSCr spectroscopy, the response of the solid to a constant stress is thermostimulated and recorded as a function of time and temperature. The return to equilibrium of the sample is characterized by parameters that can be used for defining the structure of the disordered phases.

EXPERIMENTAL PROCEDURE

The principles of thermally-stimulated creep spectroscopy principle

During the last fifteen years, TSCr spectroscopy has been used successfully to study molecular mobility in polymers [2–5]. The sample is submitted to a static mechanical shear stress σ for a time t_σ ($\approx$2 min) at a temperature T_σ, allowing the mobile units of the polymer to orientate. This out-of-equilibrium configuration (viscoelastic strain $<10^{-3}$) is then frozen by a rapid quench to a temperature T_0, much lower than T_σ, where any molecular motion is hindered, and the stress is removed.

The return to equilibrium of the sample is induced by a controlled increase in the temperature (7 K min^{-1}). The mobile units can reorient. The recovery γ, its time derivative $\dot{\gamma}$ and the temperature T are recorded versus time. The plot of the normalized magnitude, $\dot{\gamma}/\sigma$, against temperature represents the complex TSCr spectrum.

Not only does this technique permit the measurement and the characterization of the anelastic effect associated with the glass transition, but secondary retardation processes can also be observed. In addition, its low equivalent frequency (about 10^{-3} Hz) allows the resolution of overlapping energy-loss peaks, frequently met in broad, secondary retardation modes. These complex TSCr spectra can be used in an accurate comparative study of polymers; in general, an analysis of the fine structure of the complex spectra is necessary.

In polymers, the viscoelastic response is generally described with the assumption of a distribution in retardation times. The great advantage of the TSCr technique is that it allows a detailed study of this distribution. By applying the technique of fractional stresses [2, 3] in TSCr experiments, the complex spectra can be resolved experimentally into elementary spectra. The usual cycle is applied to obtain the complex spectrum, but with a narrow temperature window which allows us to obtain elementary spectra.

If the temperature window is sufficiently narrow, it is hypothesized that each experimental elementary spectrum is characterized by only one retardation time $\tau_i(T)$ following an Arrhenius equation

$$\tau_i(T) = \tau_{0i} \exp(\Delta H_i/kT) \tag{1}$$

where k is the Boltzmann constant, τ_{0i} is the pre-exponential factor, and ΔH_i is the activation enthalpy. The activation entropy ΔS_i can be deduced from τ_{0i} by the Eyring equation

$$\tau_{0i} = (h/kT) \exp - (\Delta S_i/k) \tag{2}$$

where h is Planck's constant.

In general for the observed retardation modes, the parameters τ_{0i} and ΔH_i are linked so that $\tau_i(T)$ is finally dependent on only one parameter, for example ΔH_i. Then, τ_i obeys a compensation law [2, 3]

$$\tau_i(T) = \tau_c \exp[(\Delta H_i/k)(T^{-1} - T_c^{-1})] \tag{3}$$

where τ_c is the compensation time and T_c is the compensation temperature.

The experimental points can be plotted on a compensation diagram where $\log(\tau_{0i})$ is plotted against ΔH_i in order to obtain the compensation straight lines characteristic of the structure of the amorphous phases.

Physicochemical ageing test cell

The design of the physicochemical ageing test cell has been described in detail by Dejean et al. [6]. The LDPE in the form of two 0.8 mm plaques was incorporated in a test cell of unique design in which the electrolyte was sealed between the plaques.

External contacting electrodes enabled the application of high voltages. The whole assembly was resin-encapsulated to exclude atmospheric oxygen. The test cell gives a nominally uniform electric field in the polymer sample.

RESULTS AND DISCUSSION

Reference LDPE

The TSCr set-up used for these experiments has been described elsewhere [2]. TSCr spectroscopy was applied to the characterization of the structure of LDPE in the temperature range of −180°C to 80°C. A stress $\sigma = 0.15$ MPa was applied to the sample at $T_\sigma = -73$°C for 2 min, and the viscoelastic strain obtained was frozen-in by rapid quenching to −180°C.

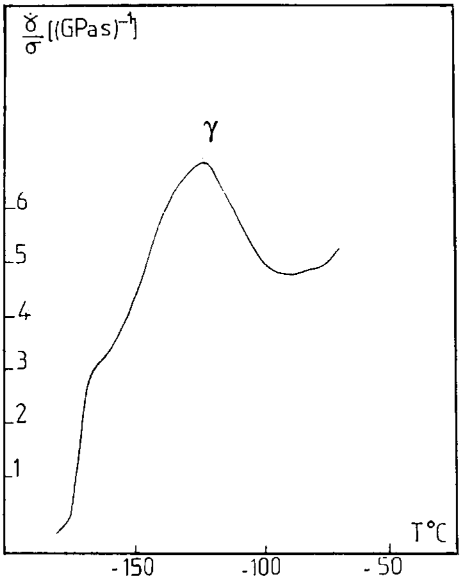

Fig. 1. Low-temperature TSCr complex spectrum of reference LDPE.

The corresponding TSCr spectrum is represented in Fig. 1. The peak situated at −125°C has been associated with the γ-mode, observed in the literature in the same temperature range either by mechanical or dielectric relaxation [7, 8].

In the same way, a stress $\sigma = 0.02$ MPa was applied to the sample at $T_\sigma = 67$°C for 2 min. In this case, the quenching temperature was −70°C.

The complex high-temperature TSCr spectrum of LDPE obtained is represented in Fig. 2. The peak at 51°C corresponds to the α-mode observed by other authors in the same temperature range [7, 8]. Note that the complex TSCr spectrum of LDPE between −180°C and 80°C does not show the β-process.

These complex spectra were resolved using the fractional stress procedure. The same stresses, $\sigma = 0.15$ MPa and $\sigma = 0.02$ MPa, were applied in the temperature ranges $-150°\text{C} < T_{\sigma i} < -50°\text{C}$ and $-50°\text{C} < T_{\sigma i} < 80°\text{C}$, respectively, with $T_{\sigma i}$ changing in steps of 5°C. The corresponding elementary spectra are reported in Figs. 3 and 4, respectively. It is interesting to note that the experimental fractional stress procedure reveals an additional peak situated around −20°C: the β-retardation mode (Fig. 3).

Each elementary peak can be characterized by τ_{0i} and ΔH_i values which can be plotted on a compensation diagram (Fig. 5) where each point corresponds to an elementary spectrum. The compensation straight lines correspond to the γ- and β-modes, in order of increasing activation enthalpies.

The fact that the retardation times in the γ-domain obey a compensation

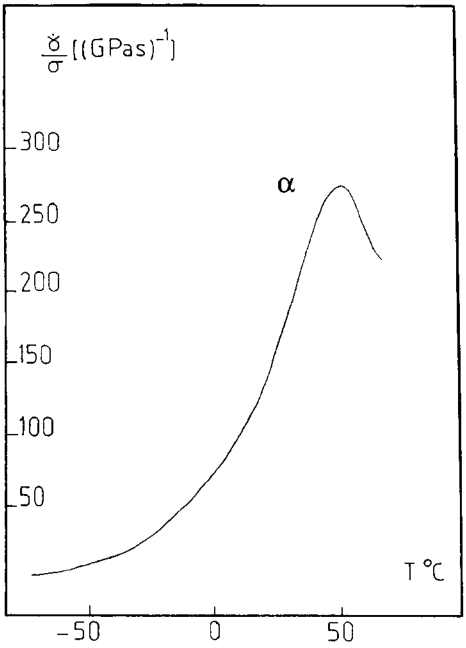

Fig. 2. High-temperature TSCr complex spectrum of reference LDPE.

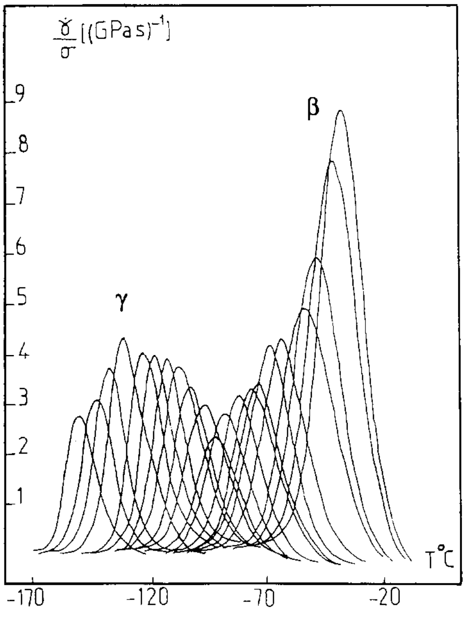

Fig. 3. low-temperature TSCr complex spectrum of reference LDPE experimentally resolved into elementary spectra.

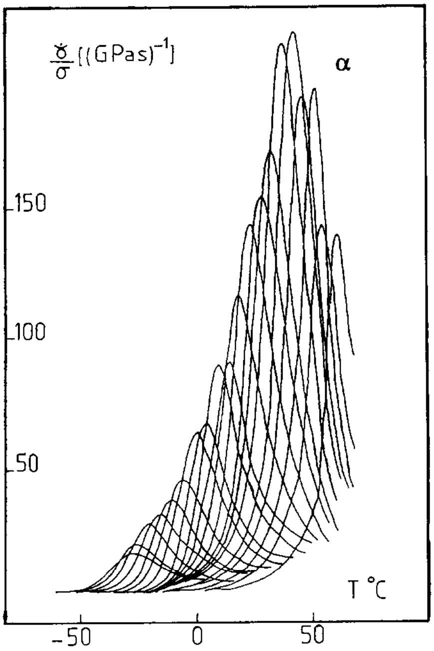

Fig. 4. High-temperature TSCr complex spectrum of reference LDPE experimentally resolved into elementary spectra.

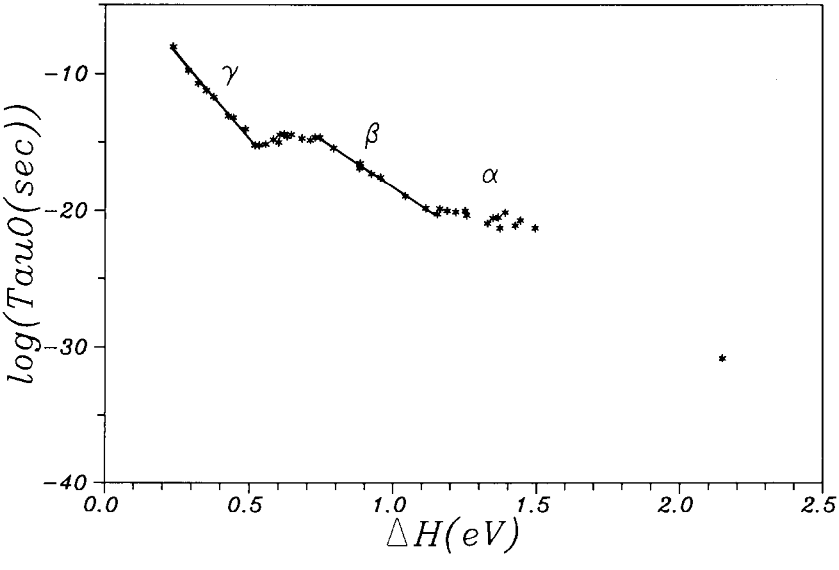

Fig. 5. Compensation diagram of reference LDPE.

law is characteristic of retardation processes in a homogeneous amorphous phase. The low values of activation enthalpies of the γ-mode are generally associated with localized movements.

The correlation between activation enthalpy and entropy for the β-mode appears at higher temperature and enthalpy than for the γ-mode. The significant width of the enthalpy distribution associated with the high values of ΔH for the β-mode suggests delocalized movements liberated at the glass transition. This has led to the conclusion that this molecular mobility is associated with the anelastic manifestation of the glass transition of LDPE.

The experimental points corresponding to the highest values of activation enthalpy correspond to the α-mode. Unlike the γ- and β-modes, they do not follow any compensation law. This result is in agreement with the assignation of this mode to molecular mobility in the rigid amorphous phase stressed by the crystallities which is not able to relax in the same way as the free amorphous phase.

INFLUENCE OF WATER AND ELECTRIC FIELD

LDPE aged with deionized water (1000 h)

The structure of the disordered phases in aged LDPE was defined by the same experimental procedure as was used for reference LDPE. All the experimental parameters were kept constant. The ageing process was performed at 75°C for 1000 h. Figure 6 shows the corresponding compensation diagram.

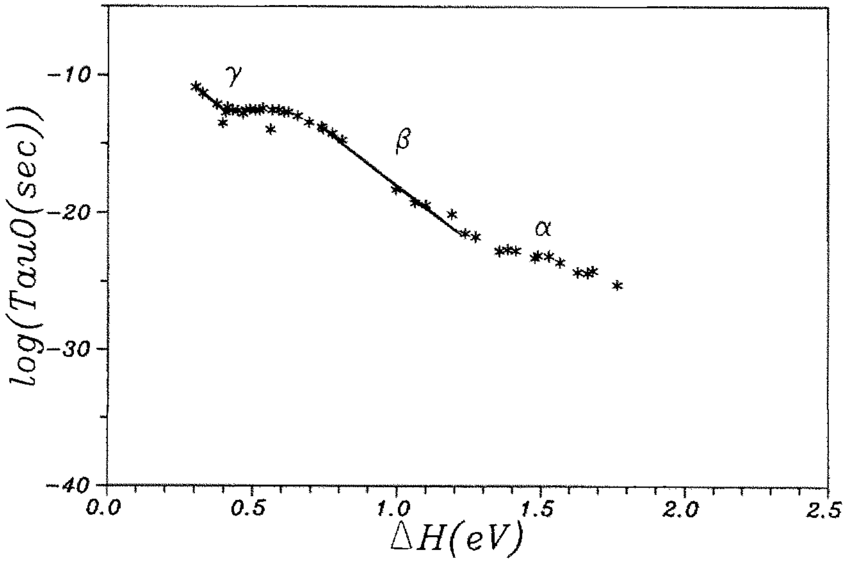

Fig. 6. Compensation diagram of reference LDPE aged (1000 h) with deionized water at 75°C.

For the γ-mode, a decrease in the activation enthalpy range is observed but there is no shift in these values. Thus, it can be assumed that there is no significant modification of the local environment of short chain sequences involved in this mode. There is a slight alignment of the α- and β-modes and a shift towards higher enthalpies of the points associated with the α-mode.

This trend in the α-mode towards a compensation phenomenon can be associated with a relaxation of the rigid amorphous phase. In this way the shift towards higher enthalpies reveals the existence of cooperative movements between the polymeric sequences of the free (β-mode) and rigid (α-mode) amorphous phases.

The slight modification of the β-mode compared to the reference LDPE can be understood if we remember that LDPE is characterized by a very low level of water absorption.

These results show an important conclusion: in the water ageing process, the rigid amorphous domains are affected before the free amorphous phase.

LDPE aged with deionized water under an electric field (1000 *h*)

This ageing was performed at the same temperature (75°C) for the same time (1000 h) but under an alternating voltage (10 kV rms 50 Hz). Figure 7 shows the corresponding compensation diagram.

The key difference from the LDPE diagrams for reference sample and polymer aged in deionized water, is the existence of three compensation

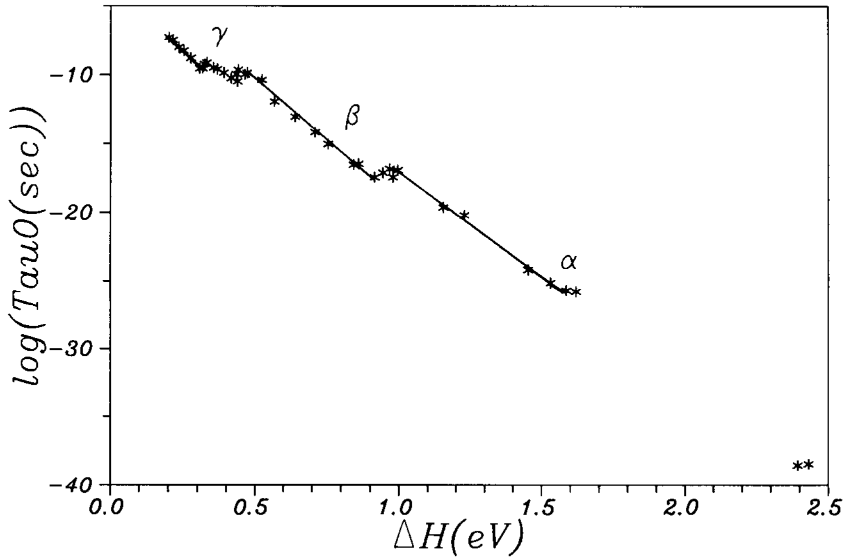

Fig. 7. Compensation diagram of reference LDPE aged (1000 h) with deionized water under an electric field at 75°C.

lines instead of two. In this case, the rigid amorphous phase (α-mode) was completely relaxed. Moreover, a significant shift towards lower values of enthalpy is observed for the three retardation modes.

A first hypothesis associates the electric field with an increase in the water diffusion process. A second hypothesis is that the local electric field might be sufficiently strong to cause the eventual breakage of polymeric chains, this is consistent with the important shift of the β-mode to lower enthalpies which can be associated with relaxation of the shorter polymeric sequences. A comparative study of Figs. 5, 6, and 7 shows the strong influence of the electric field in the ageing process. As might be expected, this process is accelerated in the presence of an electric field.

THE INFLUENCE OF IONIC SOLUTION

LDPE aged with $CuSO_4$ ionic solution under an electric field (300 *h*)

To investigate the influence of the nature of the ions, reference LDPE was soaked in a $CuSO_4$ ionic solution for 300 h under the same alternating voltage (10 kV rms, 50 Hz) and at the same temperature (75°C). Figure 8 shows the corresponding compensation diagram.

Despite the short ageing time, the behavior is qualitatively the same as that for LDPE aged in deionized water under an electric field (Fig. 7), but stronger, i.e. three compensation laws associated with the γ-, β- and α-modes and a shift of the β activation enthalpy range towards lower enthalpies.

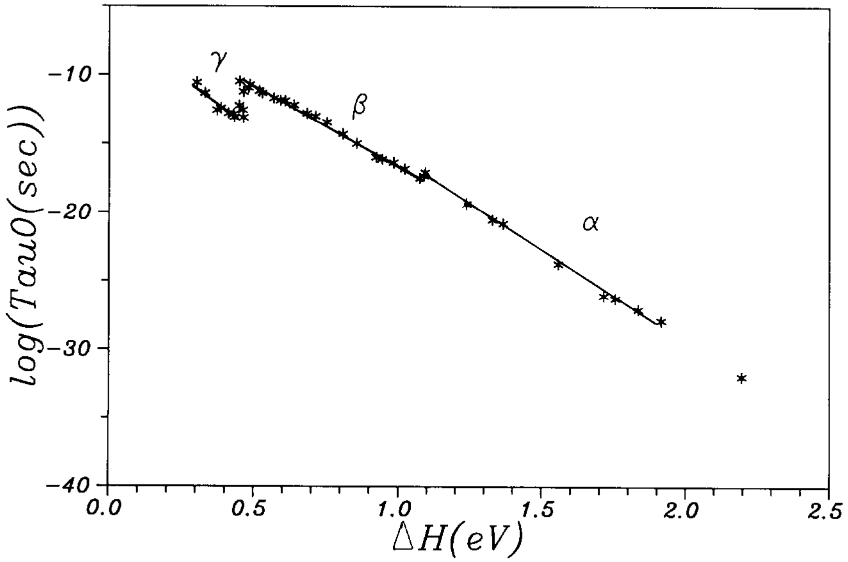

Fig. 8. Compensation diagram of reference LDPE aged (300 h) with $CuSO_4$ ionic solution under an electric field at 75°C.

It is very interesting to note the quasi-continuity of the two straight lines associated with the β- and α-modes. This behavior means that in this case there is only one compensation phenomenon associated with the β- and α-modes.

This confirms our hypothesis, associating the α-mode to the rigid amorphous phase liberated during ageing and able to relax in the same way as the free amorphous phase (β-mode).

LDPE aged with $CuSO_4$ ionic solution under an electric field (1000 h)

Reference LDPE was soaked under the same alternating voltage in the same $CuSO_4$ ionic solution at the same temperature but for 1000 h. Figure 9 shows the corresponding compensation diagram.

The pattern recorded is completely modified; this ageing process induces a destructuring of the amorphous phases of LDPE. This structural alteration may be due to interaction with the ions and would be expected to occur after the effect of the water absorption under the electric field (Figs. 6 and 7).

Ionic interactions might play the role of tie points and inhibit cooperative movements and/or relaxation processes of the amorphous phases. This results in the material becoming fragile and brittle.

LDPE aged with $KMnO_4$ ionic solution under an electric field (1700 h)

The ageing process was performed under the same alternating voltage and at the same temperature as above, but for a longer time (1700 h).

Despite the long soaking, it is important to note that the compensation diagram (Fig. 10) is only slightly different from that of reference LDPE. The α-mode is developed compared with the reference LDPE, but less strongly than for LDPE aged with deionized water under an electric field (Fig. 7) for which the effect is observed after half the ageing time.

It seems that the $KMnO_4$ ionic solution has a kind of "waterproofing" behaviour, retarding the ageing effect. This observation corresponds with the detection of morphological defects called water trees, in thin surface layers only and not in the bulk polymer [6, 9].

INFLUENCE OF TEMPERATURE

To investigate the influence of temperature, reference LDPE was soaked in the same ionic solution (NaBr) under the same alternating voltage (10 kV rms, 50 Hz) for the same ageing time (1000 h) at two different temperatures (50°C and 75°C). Figures 11 and 12 show the corresponding compensation diagrams.

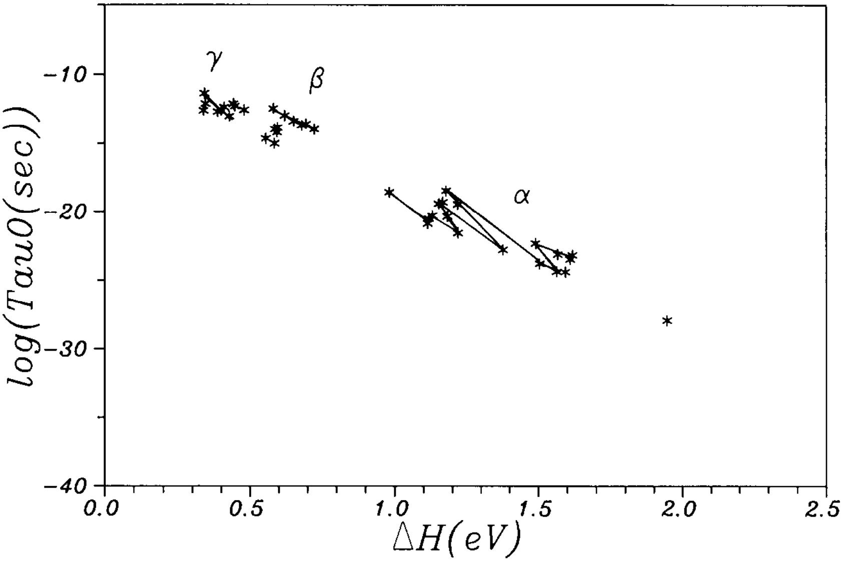

Fig. 9. Compensation diagram of reference LDPE aged (1000 h) with $CuSO_4$ ionic solution under an electric field at 75°C.

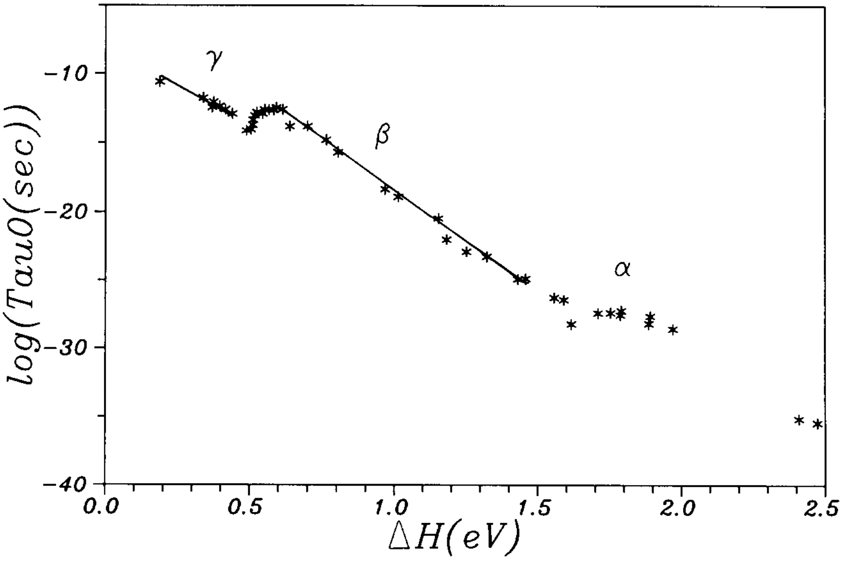

Fig. 10. Compensation diagram of reference LDPE aged (1700 h) with $KMnO_4$ ionic solution under an electric field at 75°C.

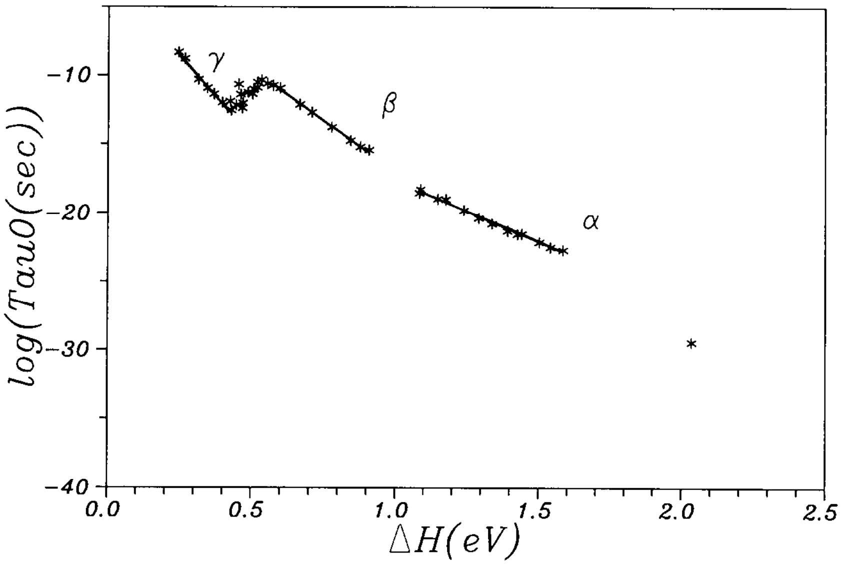

Fig. 11. Compensation diagram of reference LDPE aged (1000 h) with NaBr ionic solution under an electric field at 50°C.

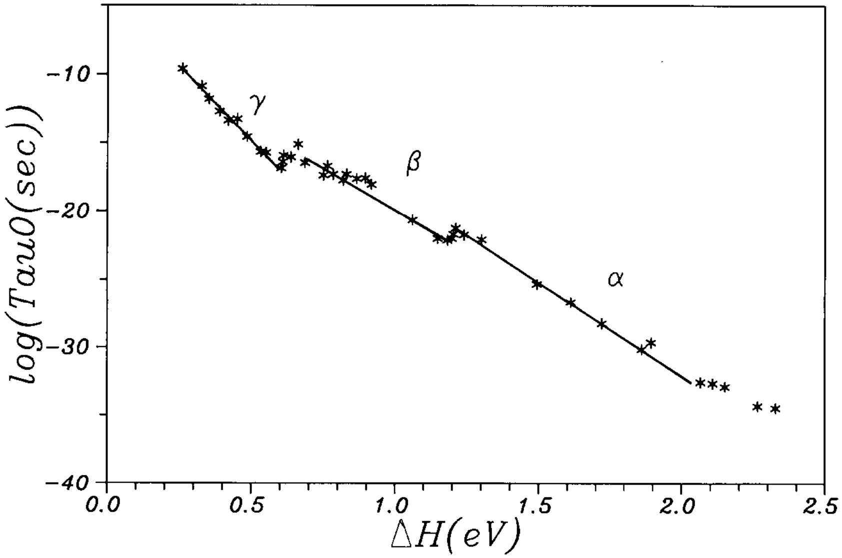

Fig. 12. Compensation diagram of reference LDPE aged (1000 h) with NaBr ionic solution under an electric field at 75°C.

These ageing conditions, particularly the electric field, allow the relaxation of all amorphous phases. Indeed, for both experiments, there are three compensation straight lines associated with γ-, β- and α-modes. As it might be expected, the ageing is stronger at 75°C than at 50°C.

For the 50°C experiment, the shift of the compensation lines towards lower enthalpies seems to confirm the previous hypothesis, i.e. an increase in water diffusion or a relaxation of shorter chains takes place after breakage of polymeric chains.

At 75°C (Fig. 12), the β- and α-modes follow the same trend, and the two compensation straight lines are almost continuous. This confirms our hypothesis associating the α-mode with the rigid amorphous phase liberated during the ageing procedure.

As in the zero-field experiment (Fig. 6), there is a shift towards higher enthalpies. However, in this case, the difference is the existence of an intermediate step (ageing at 50°C, Fig. 11). Therefore, in the ageing mechanism, after a light plastization effect there is break of polymeric chains followed by stiffening of the polymer due to some crosslinking of the short chains.

Over longer time periods, these mechanisms hinder the relaxation process of the amorphous phases. The material becomes brittle, at a rate that depends on the ionic solution.

CONCLUSIONS

These results show that thermally-stimulated creep spectroscopy is applicable to the characterization of the evolution of the morphology during physicochemical ageing in polymers.

The TSCr spectrum of LDPE is constituted of three retardation modes, designated α, β and γ in order of decreasing temperatures. The α-mode has been associated with mechanisms involving the rigid amorphous domains stressed by crystallites, while the β- and γ-modes have been attributed to the free amorphous phase.

Our experimental results show that in this kind of physicochemical ageing the rigid amorphous domains are affected before the free amorphous phase. As expected, the ageing mechanisms are accelerated in the presence of an electric field and/or by temperature increase. The comparative study of LDPE samples aged in various ionic solutions under an electric field shows the existence of a two-step process in the modification of the amorphous phases.

First a slight "plasticization" effect due to water molecules occurs, followed by breakages of polymeric chains caused by a strong local electric field; second, the polymer stiffens upon a kind of crosslinking of the chains, probably due to interactions with ionic species. Over longer times, these mechanisms hinder the relaxation process of the amorphous phases and macroscopically the material becomes brittle for ageing times that depend on the ionic solution.

We anticipate that a more thorough understanding of these ageing mechanisms will emerge from a comparative study of the same samples characterized by optical and electron microscopy and fourier transform infrared (FTIR) spectroscopy, undertaken by C. Mayoux, University of Toulouse, and by neutron activation analysis (NAA), undertaken by A. Fouracre, University of Strathclyde, Glasgow, U.K.

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