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STRUCTURE -PROPERTIES RELATIONSHIPS IN POLYMERIC MATERIALS BY THERMALLY STIMULATED CURRENT AND CREEP

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The ThermoStimulated Current (TSCu) and ThermoStimulated Creep (TSCr) spectroscopies have been applied to the investigation of amorphous phases of polymeric materials. We have analysed the molecular mobility liberated at the glass transition temperature and the compensation diagram has been used for characterizing the corresponding cooperative movements. In linear polymers, the influence of chemical and physical structures has been investigated. In polymeric networks, the evolution of the structure towards chemical composition has been shown.

Keywords: amorphous phases of polymers, ThermoStimulated Current /Creep spectroscopies

Introduction

The ThermoStimulated Current (TSCu) and Creep (TSCr) spectroscopies have been applied to the investigation of amorphous phases of polymeric materials. Since physical properties are highly dependent upon amorphous phases, a characteristic pattern of the 'structure' is particularly valuable.

First, the correlation between chemical structure and molecular mobility will be investigated.

Second, the relationship physical structure and molecular mobility will be analysed.

Third, the architecture of polymeric networks will be related to their structure.

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Methods and materials

Methods

The principle of ThermoStimulated Current/Creep is the following [1]:

– the sample is submitted to a static dielectric/mechanical stress for a time and at a temperature allowing the mobile units to orientate.

– this out of equilibrium configuration is then frozen by decreasing the temperature to LNT and the external field is cut off.

– the return to equilibrium of the sample is induced by a controlled increase of the temperature (7 $\text{deg}\cdot\text{min}^{-1}$) and the TSCu/TSCr spectrum is recorded.

In polymeric materials, the recorded spectra are complex. They can be experimentally resolved into elementary spectra by using fractional polarizations/stress [2]. Then, each elementary spectrum can be characterized by a relaxation/retardation time $\tau(T)$ following an Arrhenius equation:

$$\tau(T) = \tau_o \exp\left(\Delta H/kT\right)$$

where k is the Boltzmann constant, τ_o is the pre-exponential factor, ΔH is the activation enthalpy.

The activation entropy can be deduced from τ_o by the Eyring equation:

$$\tau_o = (h/kT) \exp -(\Delta S/k) \tag{1}$$

where h is the Planck's constant.

For the relaxation/retardation modes observed around the glass transition temperature, the parameters τ_o and ΔH are linked so that $\tau(T)$ is finally dependent only upon one parameter, for example ΔH. Then, τ obeys a compensation law [3]:

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

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

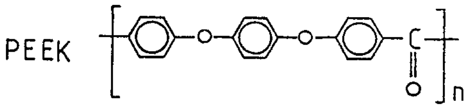
The experimental points can be plotted on a compensation diagram where log τ_o is reported *vs.* ΔH in order to obtain the compensation line characteristic of the structure of the amorphous phase.

ThermoStimulated Current experiments have been performed on a TSC/RMA from Solomat; for ThermoStimulated Creep experiments, we have used a torsion pendulum previously described [4].

Materials

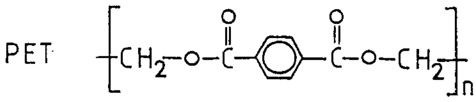
Poly(Ether Ether Ketone)

Poly(Ether Ether Ketone) (PEEK) from ICI with 10% of crystallinity has been studied. The samples were used as sheets 500 μm thick.



PolyEthylene Terephthalate

A series of PolyEthylene Terephthalate (PET) films have been prepared by Rhône Poulenc for this study.

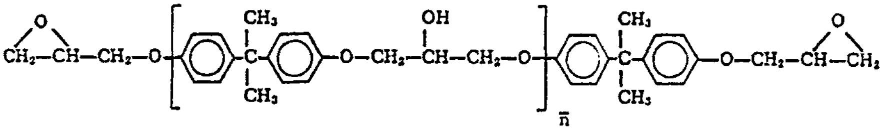


The biaxially oriented Therphane® (10 μm thick) has 39.5% of crystallinity. It was produced in a two step stretching process: the first in the travel direction; the second, of greater strain, in the transverse direction. The film was then heat set at 180°C. The biaxially oriented films has been compared with uniaxially oriented film (50 μm thick and 4% crystalline) obtained after the first process in the travel direction. The initial unoriented amorphous PET films, 150 μm thick, have also been studied as reference material.

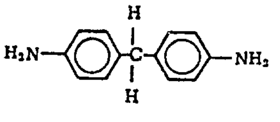
Polyepoxy

A series of polyepoxy networks resulting from the cross-linking of the diepoxide DGEBA (Diglycidyl Ether of Bisphenol A) with the primary amine DDM (4,4' Diamino Diphenyl Methane) has been investigated by TSCr. The chemical formulae of the two components are shown below.

DGEBA



DDM



The degree of condensation of DGEBA prepolymer – as determined by steric exclusion chromatography – is $n = 0.15$. In the investigated series, the amine/epoxide r ratio was varied below stoichiometric composition: $r = 1$, 0.85, 0.7 and 0.5.

Influence of chain rigidity

A comparative study of PEEK and PET has been performed in order to precise the influence of the chemical structure on the molecular mobility as exhibited in Thermally Stimulated Current spectroscopy. The TSCu spectra of unoriented PET and PEEK are represented in Fig. 1, where the normalized depolarization current i.e. the dipolar conductivity σ has been plotted *vs.* the temperature T. In both cases, the samples have been polarized for two minutes at the temperature indicated by an arrow on the figure.

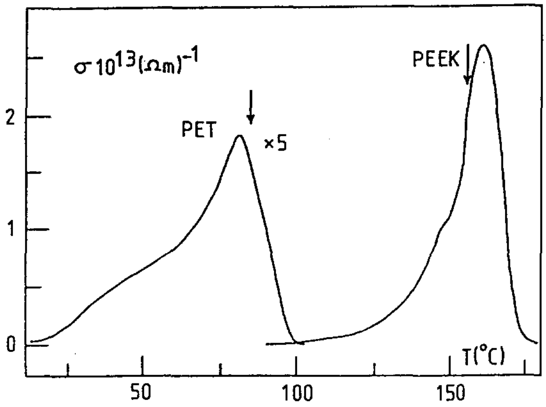


Fig. 1 TSCu spectra of unoriented PET and PEEK

For facilitating the interpretation of those TSCu peaks we have reported in Fig. 2 the Differential Scanning Calorimetry (DSC) curves of unoriented PET and PEEK: the enthalpy flow dH/dt has been reported *vs.* temperature. For both samples the characteristic step of the glass transition is followed by the crystallization peak [5]. It is evident that the TSCu peaks of Fig. 1 are the dielectric manifestation of the glass transition of unoriented PET and PEEK respectively since they are observed in the same temperature range than the DSC step. The chemical modification between PET and PEEK is responsible for the recorded spectacular shift along the temperature axis.

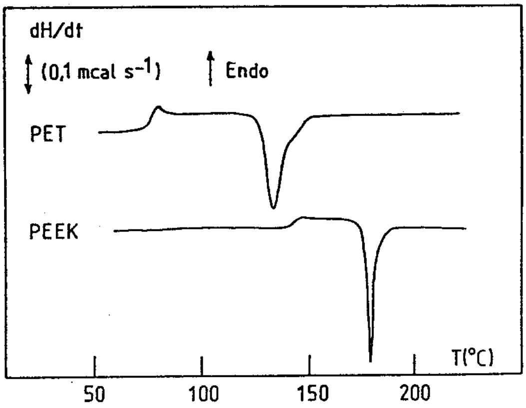


Fig. 2 DSC curves of unoriented PET and PEEK

Influence of orientation

A comparative study of PET samples with various levels of local order has been performed for illustrating the influence of orientation on the molecular mobility by TSCu spectroscopy. Figure 3 shows the TSCu spectra of unoriented amorphous PET (solid line), uniaxially oriented PET (dashed line) and biaxially oriented PET (dotted line). The various samples have been polarized for 2 minutes at the temperature indicated by an arrow in the figure. Upon orientation the TSCu maximum is shifted from 82°C (unoriented amorphous PET) to 85°C (uniaxially oriented PET) till 100°C (biaxially oriented PET). It is also interesting to note that the magnitude of the TSCu peak is significantly decreased upon increasing of crystallinity. Those peaks correspond to the dielectric manifestation of the glass transition. The shape

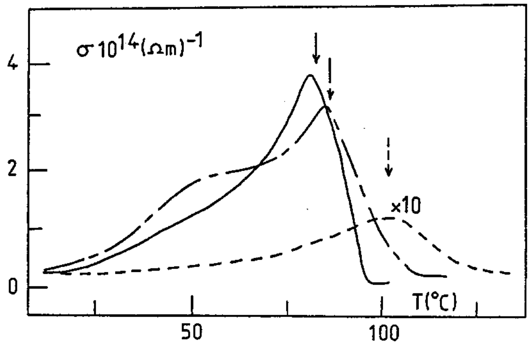


Fig. 3 TSC spectra of unoriented PET (—), uniaxially oriented PET (– —) and biaxially oriented PET (– – –)

of those peaks is also significantly modify upon orientation indicating the evolution of local order.

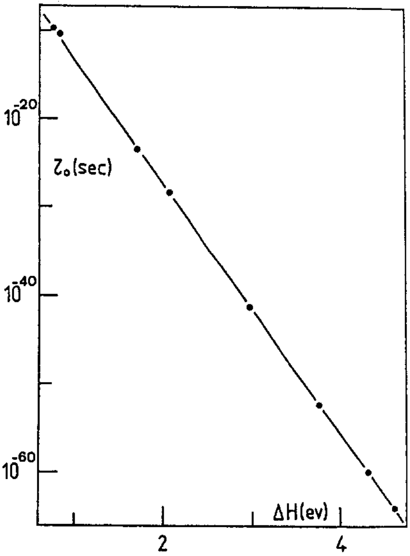


Fig. 4 Compensation diagram of unoriented PET

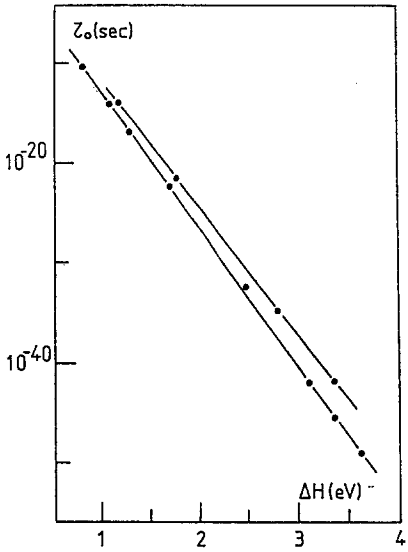


Fig. 5 Compensation diagram of uniaxially oriented PET

The dielectric relaxation time has been chosen as order parameter and its distribution has been explored by the fractional polarization technique. Figures 4, 5 and 6 show the variation of τ_o as a function of ΔH for respectively unoriented PET, uniaxially and biaxially oriented PET. In unoriented PET, a compensation line characteristic of a monophasic structure is observed. Upon uniaxially orientation, a biphasic structure is found (2 compensation lines). A new 'rigid' amorphous phase is induced upon uniaxial orientation [6, 7]. Upon biaxial orientation, this rigid amorphous phase is no longer observed since we only observe a monophasic structure. It has been postulated that the rigid amorphous phase was a precurser of the crystalline phase appearing upon biaxial orientation.

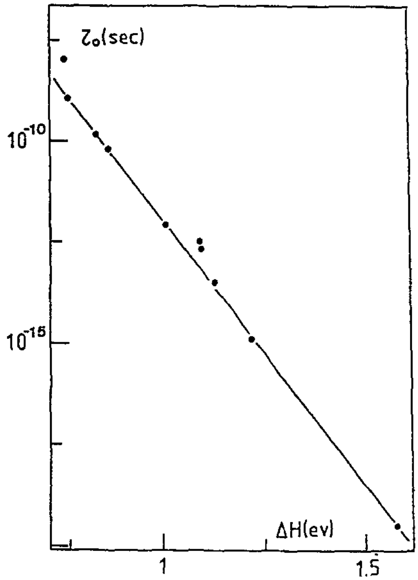


Fig. 6 Compensation diagram of biaxially oriented PET

In order to make a comparison of the evolution of local order in the 'true' amorphous phase, the corresponding compensation lines of the three PET films have been reported on the same diagram (Fig. 7): the dots and the solid line correspond to the unoriented PET, the cross and the dashed line are for the uniaxially oriented PET, the triangles and the dotted line refer to the biaxially oriented PET. It is evident that the range of the activation enthalpy is strongly restricted on the side of high values when molecular orientation increases. This result can be explained by the restriction of the true amorphous phase either by the rigid amorphous domains or by the crystallites. This observation confirms the hypothesis of the Hoffman-Williams-Passaglia model [8]; the value of the activation enthalpy reflects the size of the mobile entities.

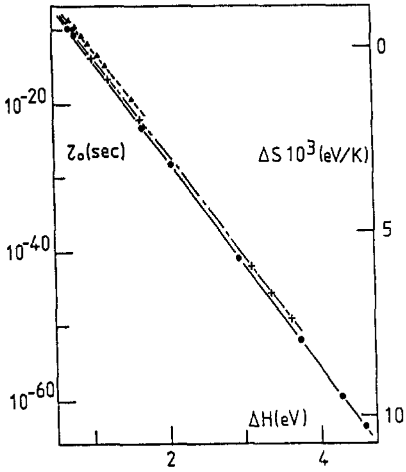


Fig. 7 Compensation diagram of unoriented PET (•), uniaxially oriented PET (+) and biaxially oriented PET (▲)

Influence of crosslink density

Epoxy-based networks have already been studied in the glass transition region [9, 10]. Here we have followed the influence of crosslink density on the high temperature retardation mode of DGEBA-DDM networks.

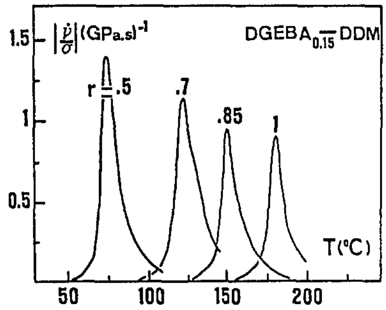


Fig. 8 Evolution of the TSCr spectrum with the amine/epoxide ratio for DGEBA (0.15)-DDM networks

Figure 8 shows the TSCr spectra obtained for the networks studied. The recovery rate $\dot{\gamma}(T)$ has been normalized to the stress σ, in order to facilitate comparison of peak heights, the loading program conditions (σ, T_σ) and the experimental results (peak temperature T_α, peak-height $[\dot{\gamma}/\sigma]$) are listed in Table 1.

Table 1 TSCr experimental conditions and experimental results for DGEBA (0.15)– DDM networks

r	σ(MPa)	T_σ(°C)	T_α(°C)	$\lvert\dot{\gamma}/\sigma\rvert$ (GPa,s)$^{-1}$
0.5	0.11	97	74	1.42
0.7	0.26	127	122	1.14
0.85	0.25	177	150	0.95
1	0.16	187	181	0.93

As r increases, the peak (labelled as α) is shifted to higher temperatures. The shift is at about 120°C between formulation $r = 0.5$ and $r = 1$. The α-peak temperature reaches its maximum at stoichiometry ($r = 1$). This result agrees quite well with those previously reported [11, 12]. This behaviour may be attributed to an important restriction of molecular mobility as the resin tends to be fully crosslinked due to an increase of the rigid phenyl groups. For thermoset resins, the evolution of the α-spectrum with r is expected to be similar to that of the glass transition; indeed, both phenomena mark the glass to rubber transition; which is associated with long range cooperative motion of the crosslinked network. This trend is confirmed by glass transition temperature measurements performed on a Perkin-Elmer DSC 2 apparatus (Fig. 9). Figure 8 also shows that the magnitude of the TSCr peak decreases with the amine-to-epoxy ratio. This effect may be assigned to higher chain mobility for the least crosslinked resins.

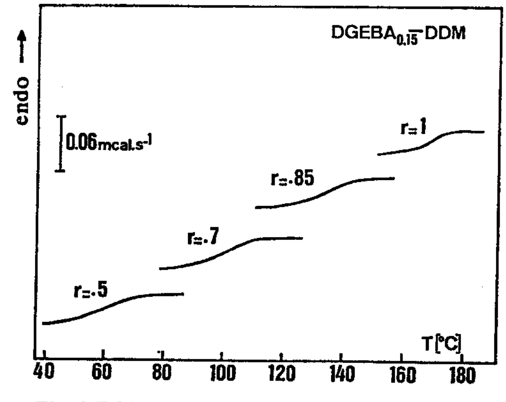


Fig. 9 DSC curves of DGEBA-DDM networks

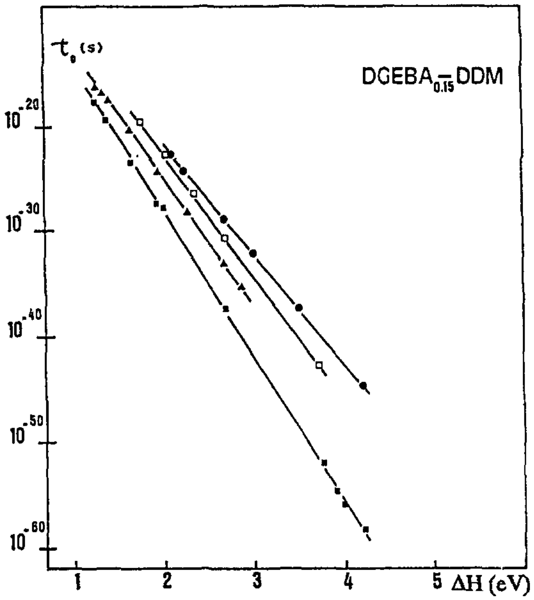


Fig. 10 Compensation diagram for the α-peak in DGEBA-DDM network: r = 1 (●), r = 0.85 (□), r = 0.7 (▲), r = 0.5 (■)

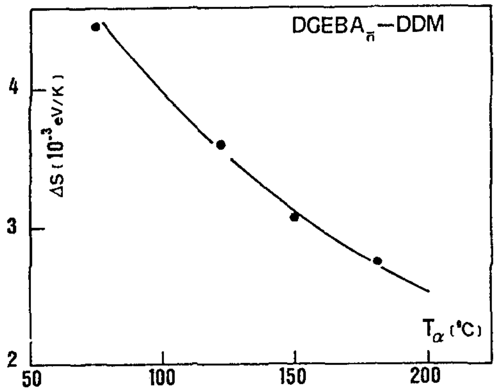


Fig. 11 Correlation between activation ΔS and peak temperature DGEBA (n = 0.15)-DDM networks

In order to investigate the microstructure of the samples each of them has been submitted to fractional stresses over the whole breadth of the corresponding peak. The investigation of the α-peak by the fractional loading technique has given the results presented in Fig. 10. This semi-logarithmic plot shows the variation of the pre-exponential factor τ_0 *vs*. the activation enthalpy ΔH for the samples under study. For each specimen, a compensation straightline is observed. The first observation in Fig. 10 is that the width of the distribution of activation enthalpy is poorly affected by the variation of r between 0.5 and 1, in spite of the 120°C shift of the α-peak (Fig. 8); in contrast, the pre-exponential factor τ_o – for a given ΔH value – increases substantially. Since τ_o is related to the activation entropy ΔS by the Eyring equation (Eq. 1), it is clear that ΔS decreases as r is increased, i.e. as the resin gets more tightly crosslinked.

By using Eq. 1, we have determined the values of the activation entropy for ΔH = 2.5 eV, and reported them against those of the peak temperature T_α (Fig. 11). ΔS decreases monotonically as T_α increases. The relatively large variation of ΔS as r varies between 0.5 and 1 compared with the slight variation of ΔH, shows that the important shift of T_α has an essentially entropic origin.

Conclusion

The Thermally Stimulated Current and Creep spectroscopies have been applied to the characterization of the amorphous phases of polymeric materials.

The structure of this phase is, of course, strongly related to the chemical structure of the polymer. The structure of the amorphous phase is also dependent upon the molecular orientation: a restriction of the size of mobile sequences is observed together with the existence of rigid amorphous domains.

For polymeric networks, the chemical composition is responsible for its architecture. In that case, the evolution of the structure is well defined by the activation entropy.

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Zusammenfassung — Mittels TSCu- und TSCr-Spektroskopie wurden amorphe Phasen von polymeren Substanzen untersucht. Es wurde die freie molekulare Beweglichkeit bei Glasumwandlungstemperatur analysiert und das Kompensationsdiagramm zur Charakterisierung der zugehörigen kooperativen Bewegungen benutzt. Bei linearen Polymeren wurde der Einfluß von chemischer und physikalischer Struktur untersucht. In polymeren Netzwerken konnte der Schritt von Strukturaufklärung zu chemischer Zusammensetzung gezeigt werden.