Viscoplastic behaviour and gelation of the solutions of a thermotropic copolyester in *m*-cresol

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The rheological properties of solutions of thermotropic 60% *p*-hydroxybenzoic acid–40% PET copolyester in *m*-cresol, in the range 2.5 to 45% of polymer concentration, are studied by means of rotational viscometry. Viscoplastic behaviour is observed at all concentrations and temperatures. The plots of the apparent yield stress against polymer concentration present maxima at 15% and minima at 25% of polymer. Above this concentration gelation takes place and the viscoelastic properties of the gels are studied by dynamic viscoelastic measurements. A model based on the inversion from isotropic continuous phase to anisotropic continuous phase is proposed to justify the results obtained. This model is supported by the fact that anisotropic micro-domains are observed by polarizing microscopy. The nature of the micro-domains is studied comparing the *FT*i.r. spectra of the solutions, the filtered solutions and the precipitate deposited in the filter.

(Keywords: solutions of thermotropics; viscoplasticity; yield stress maxima; viscoelastic gels; anisotropic micro-domains)

INTRODUCTION

Thermotropic and lyotropic liquid crystal polymers have received great attention in the literature because of their good mechanical properties and relatively easy processability. Rheological properties of these materials have been extensively reported$^{1-32}$ in order to analyse the flow behaviour from the practical and scientific point of view.

However, papers dealing with rheological properties of dissolved thermotropic polymers are scarce. This is probably due to the fact that thermotropics are, in general, difficult to dissolve and that the applications of these solutions are not immediate, although the rheology of dilute and concentrated polymer systems is always a subject of interest.

In the work described here results will be presented concerning the rheological properties of the solution of the Tennessee Eastman's 60% *p*-hydroxybenzoic acid–40% PET copolyester in *m*-cresol. It is generally accepted that this copolyester, known as X7G, was the first available thermotropic polymer, and received great attention by a number of researchers. Morphological studies$^{33-39}$ support the idea that this material is non-random with respect to chain structure, so that domains of *p*-hydroxic benzoic acid have been reported. In spite of the relatively copious literature about this copolyester, to our knowledge, no paper dealing with flow properties of solutions of this liquid crystal polymer has been published.

The purpose of the present work is to study the flow properties of the solutions of X7G in *m*-cresol, in order to try to relate the viscoplastic flow behaviour and the gelation to the formation of birefringent microdomains in the solution.

EXPERIMENTAL

The aromatic copolyester used in this study is composed of poly(ethylene terephthalate), PET, and 60 mol% *p*-acetoxybenzoic acid, PHBA. This copolymer which was developed in the seventies under the name X7G is considered to be the first reported and well characterized thermotropic liquid crystal polymer. Its inherent viscosity was i.v. $=0.68$ dl g^{-1} which, according to Jackson and Kuhfuss^{40} corresponds to $M_n \approx 20\,000$.

Solutions in *m*-cresol (Merck-Schuchart), consisting of between 2.5% and 45% of polymer, were prepared by gentle warming and stirring, taking special care to avoid water absorption by the solvent. Basic rheological measurements were carried out in a Brabender Viscotron

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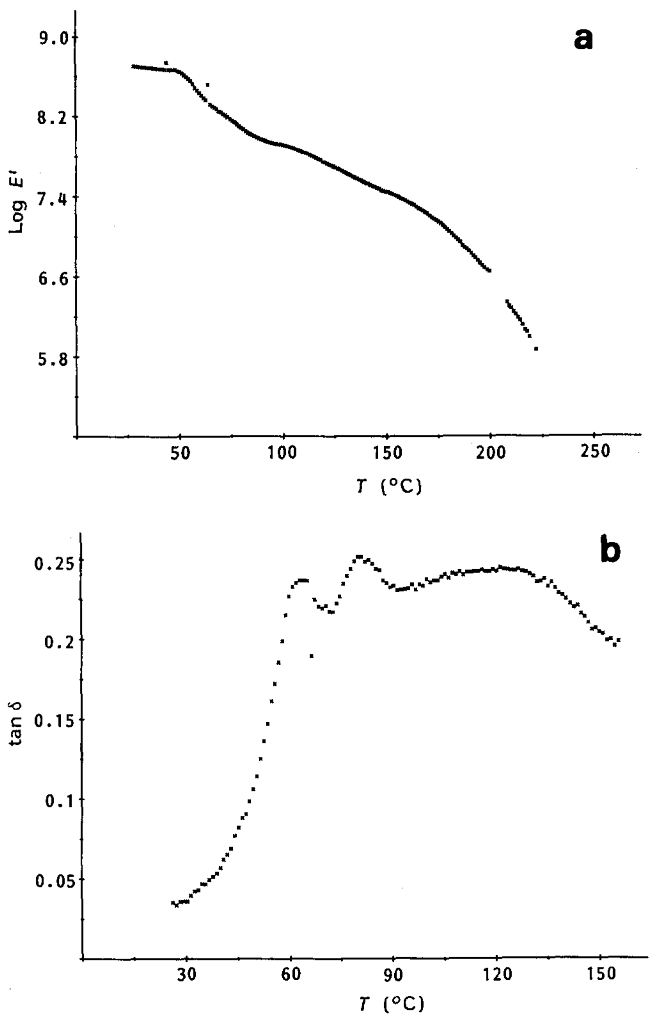

Figure 1 (a) Storage modulus, E' (Pa), and (b) loss tangent, tan δ, relaxation spectra of the original polyester, at a frequency of $\nu = 1$ Hz

rotational viscometer, using a system with $R_i = 1$ cm and $R_0 = 1.085$ cm which allows the determination of the stabilized shear stresses in a range of shear rates from $10^0\,s^{-1}$ to $10^3\,s^{-1}$. The range of temperatures was different for each concentration, but measurements for all the samples were carried out at temperatures of 70°C, 100°C and 120°C.

In order to characterize the material, storage modulus and loss tangent measurements of the copolyester were carried out in bending mode in a Polymer Laboratories DMTA apparatus. The samples were prepared by compression of the pellets at 250°C: typical dimensions were 20 × 10 × 1 mm. Measurements at frequencies of 0.1, 0.3, 1, 3, 10, 20 and 30 Hz over a temperature range of 25–200°C were collected.

At concentrations of 25% and above gels were formed by slowly cooling the solutions. The dynamic viscoelasticity of these gels was studied in shear mode (Polymer Laboratories DMTA) using disks of 12 mm diameter and 1 mm thickness. Scans of temperature at a constant frequency of 1 Hz were carried out with fresh and aged gels. Isothermal measurements at varying frequencies (from 10^{-2} Hz to 10^2 Hz) were also performed.

A Reichter polarizing microscope with a Mettler FP 52 hot stage, with a heating programme of 10°C min^{-1} and a maximum temperature of 300°C was used to analyse the original, as well as the filtered solutions. A Nicolete 5DXC *FT*i.r. spectrometer was used to analyse hot-melt pressed original copolyester and a 10% solution. The spectra were compared with those corresponding to the solution filtered through a 0.4 fine-pore glass filter and the deposited precipitate resulting from the filtering operation. Therefore four samples were analysed: original material; a solution of 10% in *m*-cresol; the 10% solution after filtration; and the precipitate deposited in the filter.

RESULTS AND DISCUSSION

Characterization

In *Figure 1* we present the storage modulus, E', and loss tangent, tan δ, relaxation spectra of the original PET/PHBA thermotropic copolyester, at a frequency of $\nu = 1$ Hz. Three relaxation peaks can be distinguished at temperatures of 63°C, 80.5°C and 125°C. The same relaxations are obtained for the rest of the frequencies. For the lowest temperature relaxation, the change with frequency is from 58°C at $\nu = 0.1$ Hz to 69°C at $\nu = 30$ Hz. For the intermediate relaxation the temperatures are 76°C at $\nu = 0.1$ Hz and 85.5°C at $\nu = 30$ Hz. The highest relaxation temperature does not change with frequency. From the plots of ln ν *versus* $1/T_{\max}$ the activation energies ΔH corresponding to the single relaxation model

$$\nu = B\exp(-\Delta H/RT_{\max}) \qquad (1)$$

are obtained. For the lowest relaxation $\Delta H = -119.2$ kcal mol^{-1} and for the intermediate transition $\Delta H = -161$ kcal mol^{-1}. These values are similar to those presented in the literature for PET/PHBA copolyesters. From dynamic mechanical measurements Benson and Lewis[39] reported three peaks at 45°C, 62.2°C and 88°C, the activation energy being 170 kcal mol^{-1} and 120 kcal mol^{-1}, respectively, for the first two relaxations. On the other hand, d.s.c. measurements have revealed the existence of transitions at 61°C and 149°C (ref. 37) and 80°C and 194°C (ref. 33).

The existence of various relaxations is interpreted as the manifestation of segmental motions in PET-rich and PHBA-rich phases of the copolyester. Actually, morphological studies carried out with other techniques like WAXS and chemical etching (with anhydrous NH_3 and n-propylamine) in conjunction with electron microscopy[35] support the idea that this material is non-random with respect to chain structure rather than completely random as it was suspected initially by the Tennessee Eastman's researchers. Domains of PHBA on the order of 0.1 to 0.8 μm and on the order of 2 to 10 μm have been reported[34–36]. On the other hand, Nicely *et al.*[38] and Benson and Lewis[39] have established that the PET-rich phase has a PET/PHBA molar ratio of approximately 1.85:1 whereas the PHBA-rich phase has a PET/PHBA molar ratio of 1:4.

The fact that the morphology of the copolymer is heterogeneous in nature is of great importance to the understanding of the rheological behaviour of the solutions, as well as the interpretation of the microscopy and *FT*i.r. spectroscopy results which will be discussed in the following sections.

Flow behaviour

Plots of the viscosity against the shear rate are presented in *Figure 2* for some concentrations at a temperature of 100°C. We call attention to two points.

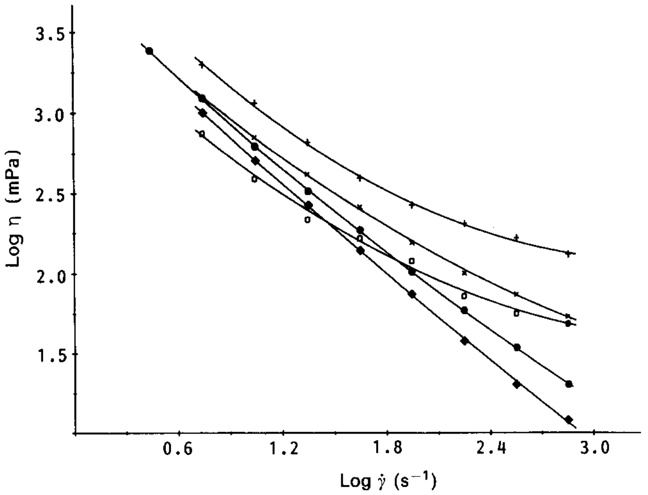

Figure 2 Plots of the viscosity (in mPa s) against shear stress (s^{-1}) for various concentrations C at a temperature of 100°C. $C=$: +, 45%; ×, 35%; □, 30%; ●, 20%; ◆, 10%

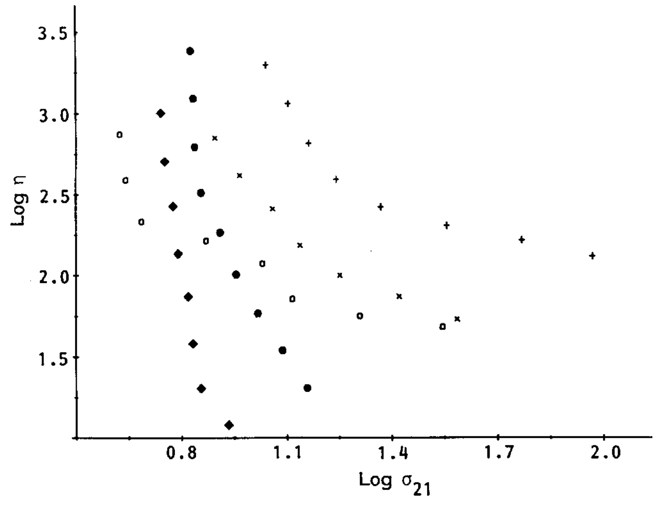

Figure 3 Viscosity (mPa s) against shear stress (Pa) for various concentrations C at a temperature of 100°C. $C=$: +, 45%; ×, 35%; □, 30%; ●, 20%; ◆, 10%

1. The flow behaviour corresponds to a plastic material rather than to the typical pseudoplasticity observed usually in polymer solutions. 2. At certain shear rates the viscosity does not increase with polymer concentration.

The plastic (viscoplastic) behaviour is better observed in *Figure 3* where viscosity is plotted against shear stress. For each concentration an apparent yield stress can be discerned below which the system acts as a solid. Pastes, slurries and suspensions are the kinds of materials which usually exhibit this type of viscoplastic behaviour, characterized by the presence of an apparent yield stress. Some empirical relations have been proposed to replace the Newtonian expression $\sigma_{21}=\eta\dot{\gamma}$. The most widely used are the Bingham[41], Casson[42] and Herschel–Bulkley[43] equations. In our case the best fits were obtained with the Casson model:

$$\sigma_{21}^{1/2}=\sigma_0^{1/2}+\eta_\infty^{1/2}\dot{\gamma} \qquad (2)$$

Plots of $\sigma_{21}^{1/2}$ against $\dot{\gamma}^{1/2}$ allow us to determine the apparent yield stress σ_0 and the so-called plastic viscosity η_∞. In *Figure 4* we present one set of plots for some concentrations at a temperature of 100°C. Similar plots are obtained for the rest of the samples. The values of σ_0 and η_∞ for all the concentrations are presented in *Table 2.*

In the case of polymers, viscoplastic behaviour is observed in filled systems[44–47], copolymers like ABS[48] and SBS thermoplastic elastomers[49], solutions of SB diblock polymer in selective solvents[50] and liquid crystal polymers[31]. In the latter case, models of domain flow have been proposed[9,51] to justify the shear thinning behaviour at very low shear rates. Nevertheless, we have

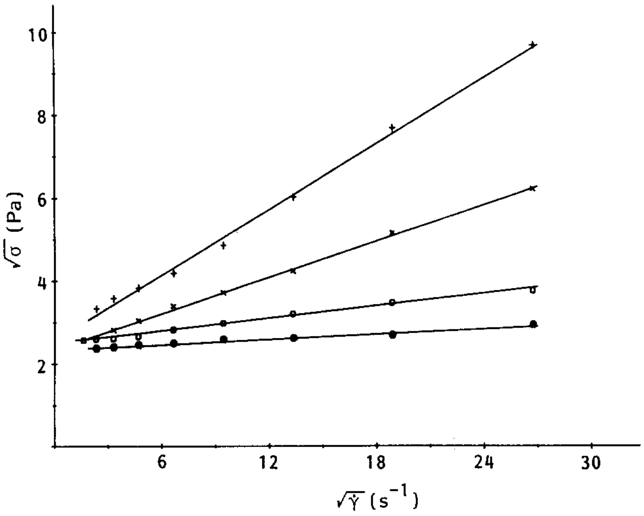

Figure 4 Experimental results adjusted to Casson model (equation 2). $C=$: +, 45%; ×, 35%; □, 20%; ●, 10%

Table 1 Values of the yield stress, σ_0, and plastic viscosity η_∞ (equation 2) for all the concentrations, at 70°C, 100°C and 120°C

C (in wt %)	T (°C)	σ_0 (Pa)	η_∞ (mPa s)
2.5	70	2.97	4.94
	100	1.77	3.94
	120	1.39	0.92
5	70	3.71	10.4
	100	3.91	2.21
	120	2.73	1.93
10	70	3.99	17.4
	100	5.42	4.76
	120	4.786	2.401
15	70	8.22	38
	100	7.83	15.4
	12	6.94	10.8
20	70	6.38	81.2
	100	6.25	25.6
	120	3.94	27.9
25	70	0.85	223
	100	0.79	81.8
30	70	7.03	1440
	100	2.51	254
	120	2.89	104
35	70	6.90	582
	100	5.51	220
	120	3.71	110
40	70	7.30	1098
	100	4.86	426
	120	1.49	316
45	70	15.65	1680
	100	6.54	696
	120	1.33	464

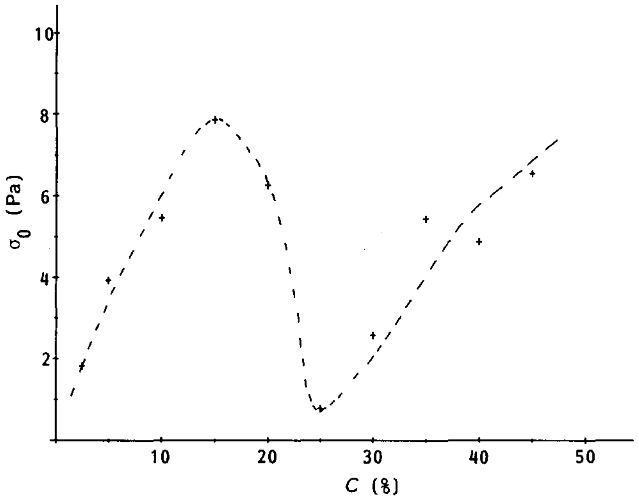

Figure 5 Yield stress σ_0 (Pa) as a function of polymer concentration at a temperature of 100°C

to point out that in some liquid crystal polymers this rheological phenomenon is not observed; yield stress only appears when phase separation takes place.

Another well known rheological characteristic of the lyotropic polymer liquid crystal polymers is the sudden change in viscosity with increasing polymer concentration[7,22,24,26,32]: an abrupt rise in viscosity is followed by a falling branch corresponding to a drop of η with increasing concentration. As has been seen in many cases, this particular behaviour of the viscosity as a function of concentration depends on the shear strain at which the viscosity is taken. Usually at high shear strains the presence of a maximum disappears but the opposite behaviour has also been reported (see Figure 2 in ref. 18).

To our knowledge very few researchers have treated the liquid crystal polymers as viscoplastic materials and adjusted the rheological results to the Bingham[41], Herschel–Bulkley[43] or Casson[42] models. In this sense we draw attention to the work by Horn and Kléman[52] analysing the effect of disordered texture.

In our case we have plotted the apparent yield stress σ_0, obtained according to the Casson[42] equation, as a function of polymer concentration. As can be seen in *Figure 5* the behaviour is similar to that reported for the viscosity in lyotropic systems: σ_0 increases up to 15% and then decreases sharply presenting a minimum at 25%. Taking into account the heterogeneous character of the copolymer, we have interpreted the results in *Figure 5* as a consequence of a two-phase morphology of the X7G/*m*-cresol system. We have considered literature cases of η *versus* concentration plots presenting maxima at a certain concentration, including dispersions[53], emulsions[46,54], two-phase polymer blends[55,61] and lyotropic polymer liquid crystals[22]. There is a great similarity between the morphology of the lyotropic systems studied by Aharoni (polyisocyamides[20] and polyisocyanates[21], in which the anisotropic phase adopts the form of spherical droplets suspended in an isotropic medium) and our thermotropic copolyester/*m*-cresol solutions. In *Figure 6* we present polarized light micrographs for 10% and 25% concentrations of polymer. An isotropic phase containing microscopic anisotropic spherulites is observed at 10% whereas at 25% anisotropic phase prevails. Due to the similarity of the morphologies we have applied a modification of the model proposed by Aharoni[22], to our results of *Figure 5* (up to 25%).

We assume that in the isotropic solution, there is no birefringent microdomain so the volume of the discrete anisotropic phase is $V^{a}_{inc}=0$. On the other hand, we assume that at 26% the solution is anisotropic, so there is no isotropic inclusion and therefore, $V^{i}_{inc}=0$. Between these two boundaries the solution behaves as a two phase isotropic–anisotropic (or anisotropic–isotropic) system. Following Aharoni[22] we can consider that the apparent yield stress (a.y.s.) of both phases drops in a non-linear convex way from the values at which $V^{a}_{inc}=0$ to $V^{i}_{inc}=0$.

Starting from the isotropic phase and increasing the volume of the discrete (anisotropic) phase gives rise to the equation

$$\begin{array}{ll} \text{isotropic} & (\sigma^{i}_{inc})^2=(\sigma^{0}_{inc})^2(1-V_{inc})+(\sigma^{1}_{mat})^2V_{inc} \\ \text{matrix} & (\sigma^{i}_{mat})^2=(\sigma^{0}_{mat})^2(1-V_{inc})+(\sigma^{1}_{inc})^2V_{inc} \end{array} \qquad (3)$$

where σ^{i}_{inc} represents the a.y.s. of the inclusions (anisotropic microdomains, in this case) and σ^{i}_{mat} is the a.y.s. of the matrix (isotropic phase, in this case). σ^{0}_{inc}, σ^{0}_{mat}, σ^{1}_{mat} and σ^{1}_{inc} are adjustable parameters.

When the phase inversion from anisotropic inclusions in an isotropic matrix to isotropic inclusions in an

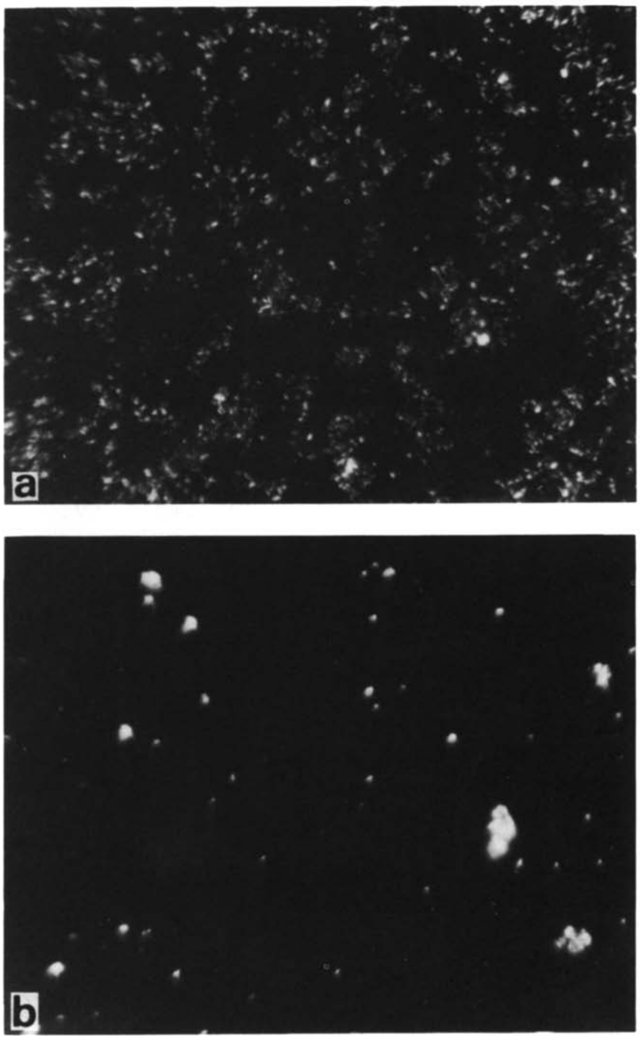

Figure 6 Polarized light micrographs of (a) 25% and (b) 10% concentration of polymer samples at 100°C

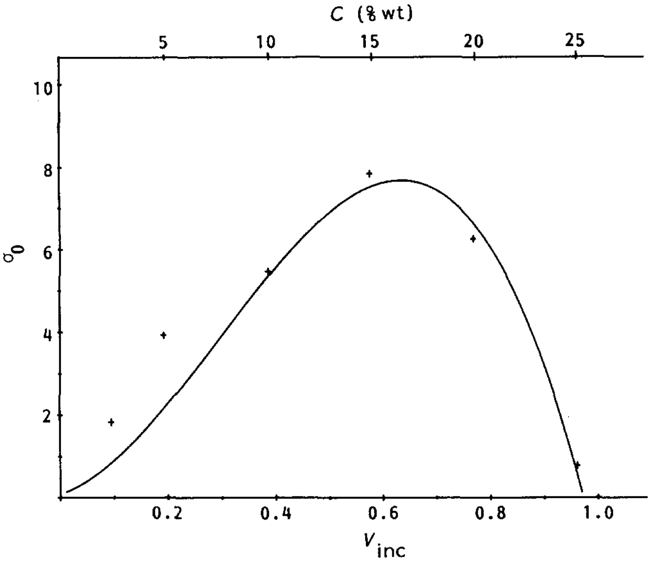

Figure 7 Comparison of the experimental data of σ_0 with the values obtained from equation (5)

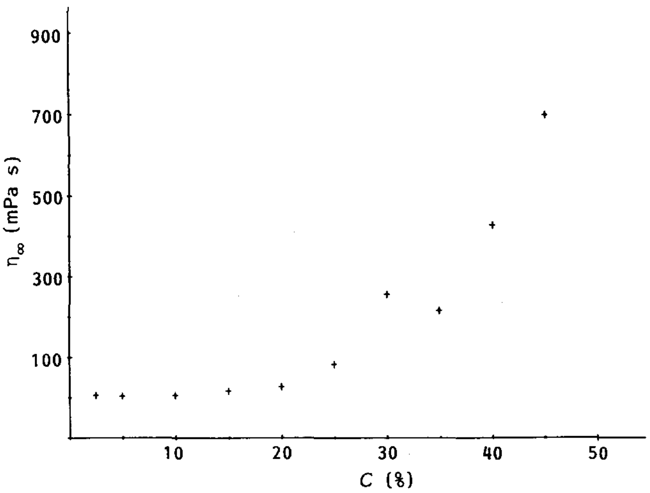

Figure 8 Plastic viscosity of the Casson model against polymer concentration ($T = 100°C$)

anisotropic matrix occurs the equations are:

$$\begin{array}{ll} \text{anisotropic} & (\sigma^{a}_{inc})^2 = (\sigma^{1}_{inc})^2(1 - V_{inc}) + (\sigma^{0}_{mat})^2 V_{inc} \\ \text{matrix} & (\sigma^{a}_{mat})^2 = (\sigma^{1}_{mat})^2(1 - V_{inc}) + (\sigma^{0}_{inc})^2 V_{inc} \end{array} \qquad (4)$$

Now σ^{a}_{inc} represents the a.y.s. of the isotropic inclusions whereas σ^{a}_{mat} is the a.y.s. of the anisotropic matrix.

In these equations we have used the following values for the adjustable parameters: 3 Pa for the a.y.s. of the anisotropic inclusions in the isotropic matrix σ^{0}_{inc}; 0.8 Pa for the a.y.s. of the isotropic matrix σ^{0}_{mat} (obtained from extrapolation of experimental data) σ^{1}_{mat}; 0.4 Pa for the a.y.s. of the isotropic inclusions in the anisotropic matrix σ^{1}_{inc} and 0.6 Pa for the a.y.s. of the anisotropic matrix σ^{1}_{mat} (from extrapolation of experimental data).

Attempts to establish the dependence of the apparent yield stress with the concentration of the dispersed phase have been reported in the literature[62,63]. Among the equations proposed we have selected the following[64]:

$$\sigma_0 = k\omega \exp(b\omega) \qquad (5)$$

where ω is the weight fraction of the disperse phase and k and b are adjustable parameters.

In our case we have taken $k = 8$ Pa and $b = \sigma_{mat}/\sigma_{inc}$, as obtained according to equations (3) and (4). The comparison of the experimental data with the values obtained from equation (5) are presented in *Figure 7*. The phase inversion takes place at approximately $V_{inc} = 0.7$.

*Viscoelasticity of X7G/*m-*cresol gels*

Above the concentration of 25% the rheological behaviour of solutions is completely different, as gelation takes place. The yield stress increases with the increasing presence of polymer (*Table 1* and *Figure 5*). As can be seen from *Figure 8*, the viscosity η_∞, which remains almost constant up to 20%, increases, showing a dependence of a power of 4 with concentration. But the most clear evidence of the occurrence of gelation at high concentrations is given by dynamic viscoelastic measurements, presented in *Figures 9* and *10*. The fact that G' remains constant (*Figure 9*) and that the complex viscosity $\eta^* = [(G'/\omega)^2 + (G''/\omega)^2]^{1/2}$ varies as the inverse of the frequency, is typical of solid elastic systems including gels based on networks of non-covalent bonds[65–70]. On the other hand (*Figure 10*) the existence of a plateau zone at low temperatures and the decreasing values of G' and increasing values of tan δ as temperature

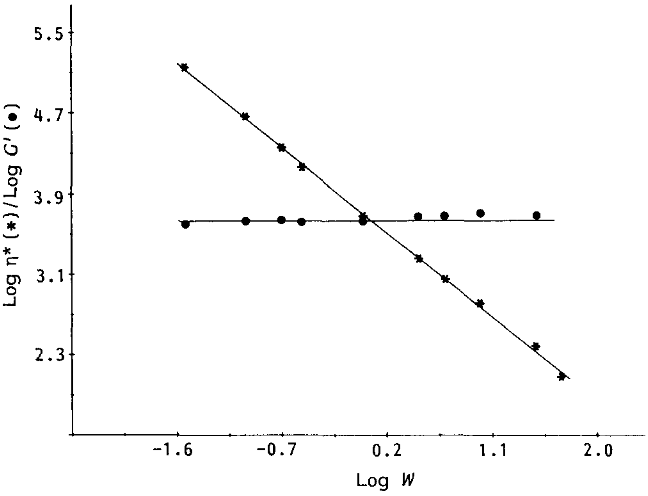

Figure 9 Shear storage modulus, G' (Pa) and complex viscosity η^* (Pa s) (see text) as a function of frequency, for 30% polymer concentration at $T = 21°C$

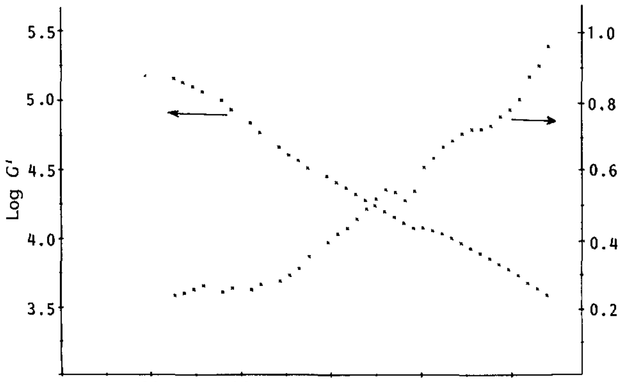

Figure 10 Shear storage modulus and loss tangent, taken at $\nu = 1$ Hz, as a function of temperature, for 40% polymer concentration

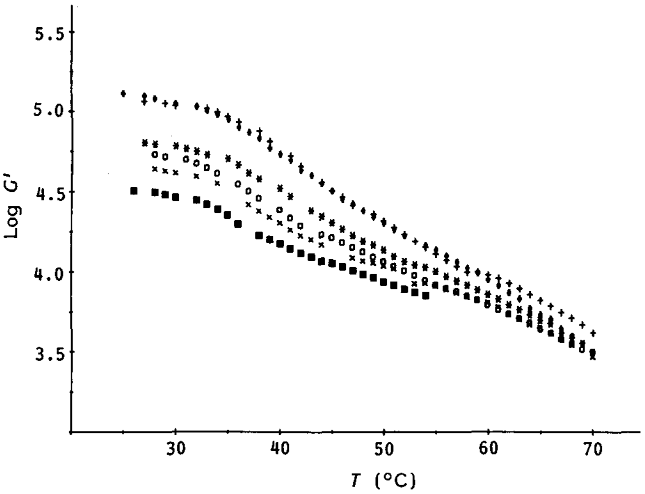

Figure 11 Effect of time on shear storage relaxation spectrum, for 40% polymer concentration. *T*: ■, 1 h; ×, 3 h; □, 6.5 h; ∗, 24.5 h; ◆, 5 days; +, 11 days

increases is characteristic of thermoreversible gels and reflects the beginning of the fusion of the system.

It is also worth pointing out the effect of aging in storage modulus, presented in *Figure 11*. It takes some days (depending on polymer concentration) to obtain repetitive values of *G'*. The influence of concentration on aged gels in the range considered in this work can be expressed by a power relation $G_e \propto C^4$, a result which is similar to that reported for some thermoreversible gels.

In many gels the nature of the linkages of the network giving rise to the elasticity remains unknown. In the case of gels based on cellulose nitrate, polyacrylonitrile, poly(vinyl chloride)[71] and polystyrene[72], crystallites would act as junctions, although in the latter case other possibilities are also suggested[73].

The presence of crystalline domains observed by microscopy (see *Figure 6*) makes the situation of X7G/*m*-cresol gels rather similar to the PVC based gels. We must call attention to the fact that in our system H-bonds are likely to occur[74], between carbonyl groups of the chain backbone and hydroxyl hydrogens of the solvent. Actually this type of interaction has been detected by i.r. spectroscopy in the case of X7G solved in hexafluoro-2-propanol[75].

The ageing effect observed in *Figure 11* is also similar to the influence of time on *G'* noticed in PVC based gels[70], for which the development of a polymer-rich and a polymer-poor region is proposed.

Nature of the birefringent micro-domains

In the case of 50:50 mixtures of poly(ethylene terephthalate) and X7G, it has been reported[76] that when both polymers were dissolved in *o*-chlorophenol at 60°C, the insoluble part (removed by filtration) consisted of crystalline poly(*p*-oxybenzoate).

Taking into account this result, we have tried to identify the nature of the microdomains observed in *Figure 6* by means of *FT*i.r. spectroscopy of the solution, the filtered solution, the precipitate deposited in the filter and the X7G copolyester. This is presented in *Figure 12*. The spectrum of the solution is not included for clarity in distinguishing the curves.

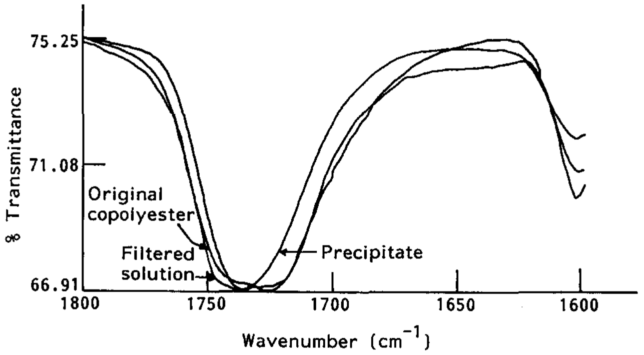

Figure 12 *FT*i.r. spectra of the original copolyester, the 10% filtered solution and the precipitate deposited in the filter (see text)

In order to compare the spectra the most interesting zone is the one corresponding to the absorption of the carbonyl group, between 1750 and 1720 (cm^{-1}). We draw attention to the following remarks. For the original X7G copolyester two absorption bands are observed at 1737 cm^{-1} and 1727 cm^{-1}, corresponding to the two types of carbonyl present in the sample. The same bands are observed for the filtered solution and the unfiltered solution, respectively, even though the latter are not presented in *Figure 12*. For the precipitate deposited in the filter, however, only one absorption band, at 1737 cm^{-1}, takes place. This indicates that only one of the components (PHBA) is present in the precipitate.

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