

**RHEOLOGY AND PHASE BEHAVIOUR
OF THE SYSTEM PBZT-PHOSPHORIC ACID-WATER**

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| 13. ABSTRACT (Maximum 200 words) Our assignment was to map out the viscosity of PBZT in a suitable solvent as a function of temperature, concentration, and shear rate. The richness and associated complexity of the system, however, forced us to place the matter in a much broader framework. Which, thanks to our wide ranging and possibly unique experience into this system, we were in a position to do. As PBZT is difficult to dissolve the choice of solvent is very limited. The most common is polyphosphoric acid used also in synthesis, characterization and processing. This solvent, as our studies have shown, is itself a complex system of polyphosphoric acids of different degrees of polycondensation and water in equilibrium, itself affected by temperature. In fact, in the polycondensation degrees used in the processing of PBZT, it is a mixture of orthophosphoric acid (OPA) and diphosphoric acid (DPA). This, with PBZT as a solute, gives rise to a complex phase diagram involving a variety of phases as previously investigated here. Any meaningful interpretation of measured viscosity values will need to refer to this phase diagram, the variation of viscosities with temperature and concentration (and to a lesser extent with strain rate) is strongly related to the phase behavior. | | | | |
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INTRODUCTION

Our assignment was to map out the viscosity of PBZT in a suitable solvent as a function of temperature, concentration and shear rate. This will form Part I of the report. The richness and associated complexity of the system, however, forced us to place the matter in a much broader framework. Which, thanks to our wide ranging and possibly unique experience into this system arising from our previous commitments on the ERO/AFO Grant, we were in a position to do. This latter extension of the work is contained by Part II of the present report. The common background to Parts I and II is as follows.

As PBZT is difficult to dissolve the choice of solvent is very limited. The most common is polyphosphoric acid used also in synthesis, characterization and processing. This solvent, as our studies on the ERO/AFO Grant have shown, is itself a complex system of polyphosphoric acids of different degrees of polycondensation and water in equilibrium, itself affected by temperature. In fact, in the polycondensation degrees used in the processing of PBZT, it is a mixture of orthophosphoric acid (OPA) and diphosphoric acid (DPA). This, with PBZT as solute, gives rise to a complex phase diagram involving a variety of phases as previously investigated here (see Figure 4 below). Any meaningful interpretation of measured viscosity values will need to refer to this phase diagram, the variation of viscosities with temperature and concentration (and to a less extent with strain rate) is strongly related to the phase behaviour.

PART I: VISCOSITIES

The measurements were carried out using a rheometrics R 800 with a cone-plate geometry, cone angle 0.1 rad and diameter of 0.5 in. Here the solutions were sheared between the conical gap enclosed by the cone and plate at a constant variable shear rate, and the stress determined through measurement of the torque exerted onto the suspended outer cylinder. For all experiments a transient mode with an application of steady shear, until a constant stress level appeared, was applied. The experiments were done under dry nitrogen environment. The primary information is the stress versus shear rate relation at a given temperature and concentration which, itself can also be a function of the time of the shear application. This information is contained in the Figures 2, 3, 5, 6, 7, 8 and 9 below. From this data the viscosity is extracted by forming the stress/strain ratios at approximately stable region of the curves (plateaus). As will be clear the viscosity so defined includes only a fraction of the information obtained in course of the full work, the latter thus extending far beyond the originally defined objectives.

Table 1 contains viscosity data as derived from the full work underlying this report.

Table 1: RHEOMETRICS DATA/ Viscosities (Pa*s)

| sample | temperature | shear rate (s ⁻¹) | | | | | | |
|-------------|-------------|-------------------------------|------|-----|-----|-----|----|-----|
| | | 0.01 | 0.1 | 1 | 3 | 5 | 10 | 100 |
| OPA/PA, | 25 °C | 5 | 13 | 48 | | | 41 | 41 |
| PBZT 2%, | 30 °C | | 30 | 60 | 70 | | | 2 |
| | 60 °C | | 2000 | 500 | 20 | | | 0.2 |
| | 100 °C | | 1000 | 500 | 220 | | | 20 |
| PBZT 3.4%, | 30 °C | | 3000 | 170 | 200 | | | 100 |
| | 60 °C | | | | 24 | | | 2.5 |
| | 80 °C | | | | 23 | | | 50 |
| | 100 °C | | | | 55 | | | 0 |
| PBZT 4.6 %, | 30 °C | | | 170 | 45 | | | 45 |
| | 60 °C | | | 100 | 45 | | | 0.5 |
| | 80 °C | | 500 | | 10 | | | 0 |
| | 100 °C | | 1200 | | 3 | | | 0.5 |
| | 120 °C | | | | 30 | | | 0 |
| | 160 °C | | | | | | | 1 |
| PBZT 6%, | 80 °C | | | 300 | 85 | | | 15 |
| | 100 °C | | 1400 | 350 | 160 | | | 35 |
| PBZT 9%, | 30 °C | | 1500 | 450 | 200 | | | 120 |
| | 60 °C | | 80 | 31 | 120 | | | 30 |
| | 100 °C | | 66 | 260 | 130 | 100 | | 28 |

The first row gives viscosity values for the pure solvent at different shear rates as derived from Figure 2 and plotted out explicitly in Figure 1. Subsequent rows give the viscosities for PBZT solutions at different concentrations each at several temperatures again as a function of shear rate.

In this Part I we are only concerned with viscosities defined as the stress/strain ratio, providing a measure of the fluidity of the system under the relevant conditions (temperature, concentration, strain rate) without any reference to the underlying complexity or homogeneity of the system. As such it should serve as a guide to engineering applications providing an assessment of the stress input required for a given flow rate or, the flow rate produced through a given stress input. However, without relating this

information to the phase diagram (Figure 4, Part II below) little trend or regularity can be seen.

Thus, the pure solvent first shows an increase in viscosity with shear rate, which in rheological terms refers to shear thickening. Nevertheless for sufficient high shear rates the viscosity becomes invariant (Figure 1) with shear, as appropriate to a Newtonian liquid, (the latter also born out by instantaneous stress relaxation on cessation of shear, Figure 2 and 3 below).

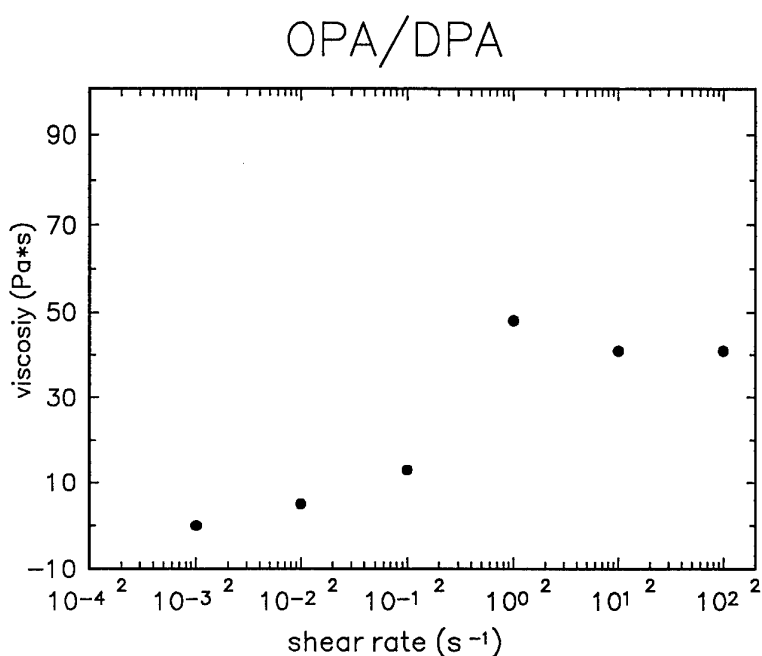


Figure 1: Plot of viscosity vs. shear rate, OPA/DPA, 25 °C

The solutions of PBZT showed a more complex pattern of behaviour as expressed in terms of viscosity. They showed shear and time dependence simultaneously. We observed large drops in viscosity with shear (in rheological terms shear thinning) particularly at low shear rates (Figure 6) and a slow decay in stress on cessation of shear (Figure 5). Such effects are characteristic features of viscoelastic fluids displaying elastic retardation and memory effects. It will be apparent that any attempt to characterize such

systems by the single parameter viscosity will be of limited usefulness. Even so the values are contained in Table 1 for the record. Gaps in Table 1 relate to conditions of unusual anomalous behaviour or of less importance. However, even in these cases the full information on flow behaviour (more specifically response to shear stress) is contained in the graphs presented in Part II below. In addition a totally new and unusual effect became apparent as stated below.

PART II: FLOW BEHAVIOUR IN TERMS OF THE PHASE DIAGRAM OF THE PBZT-OPA/DPA-WATER SYSTEM

Shear experiments were performed in order to confirm the established phase diagram of the system PBZT-OPA/DPA-WATER.

First experiments were carried out using only the solvent system. Figures 2-3 show the results.

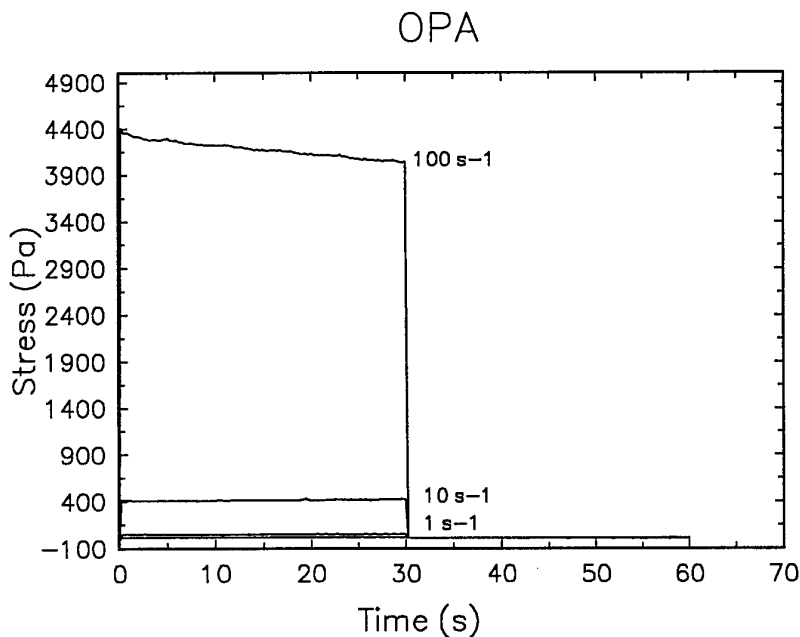


Figure 2: Plot of stress vs. time for different shear rates, OPA/DPA, 25 °C

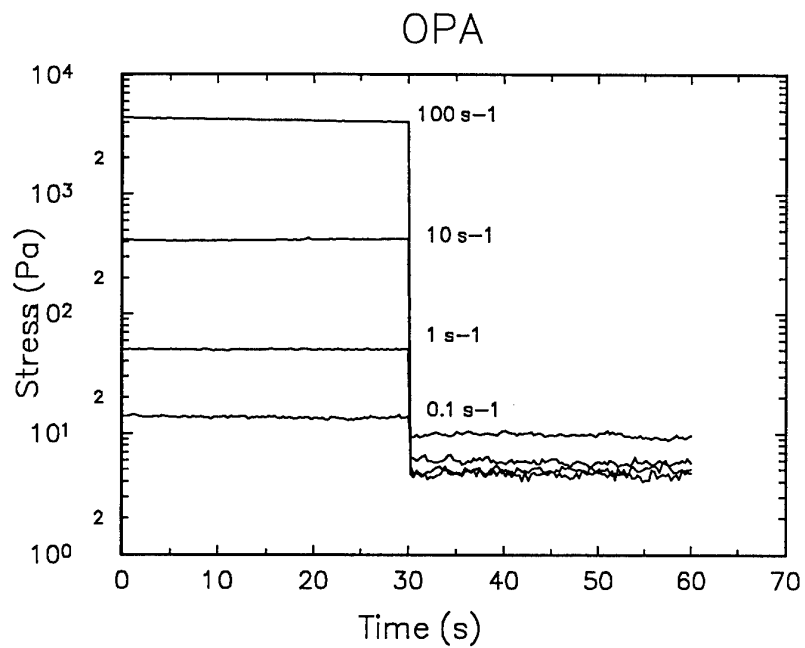


Figure 3: Plot of stress vs. time for different shear rates, OPA/DPA, 25 °C

Although a shift of the phase transition temperatures of the phase diagram during an application of shear is very likely and possible, the principal picture of the phase diagram should remain similar to that investigated before (see Figure 4, Fischer, Odell, Murray and Keller).

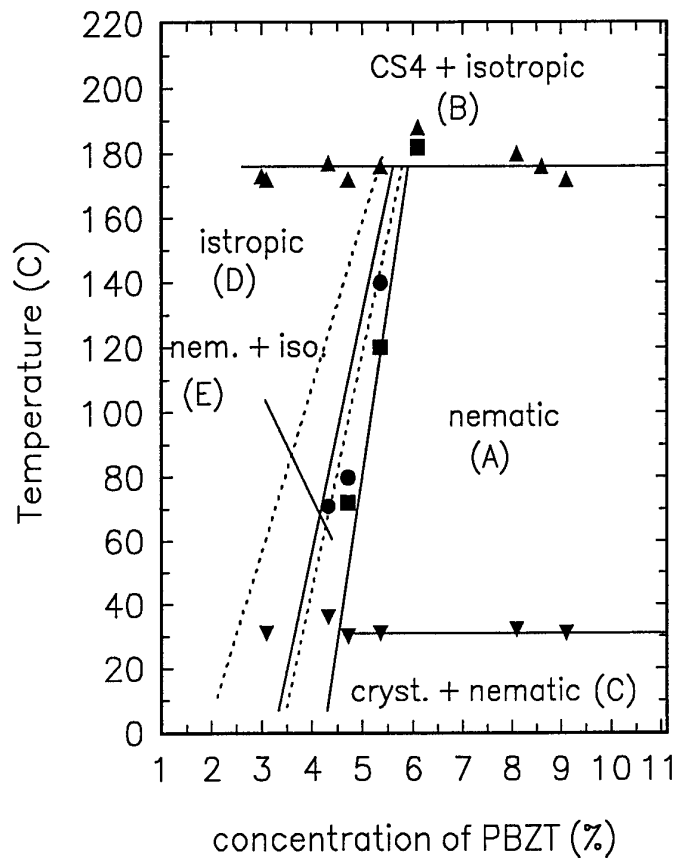


Figure 4: Phase diagram of PBZT in OPA

An isotropic solution of the polymer (2 %) shows the following behaviour. After application of shear the stress initially builds up and then decreases constantly to a very small remaining level possibly due to alignment of the rigid macromolecules (see Figure 5). The relaxation is instant and very fast.

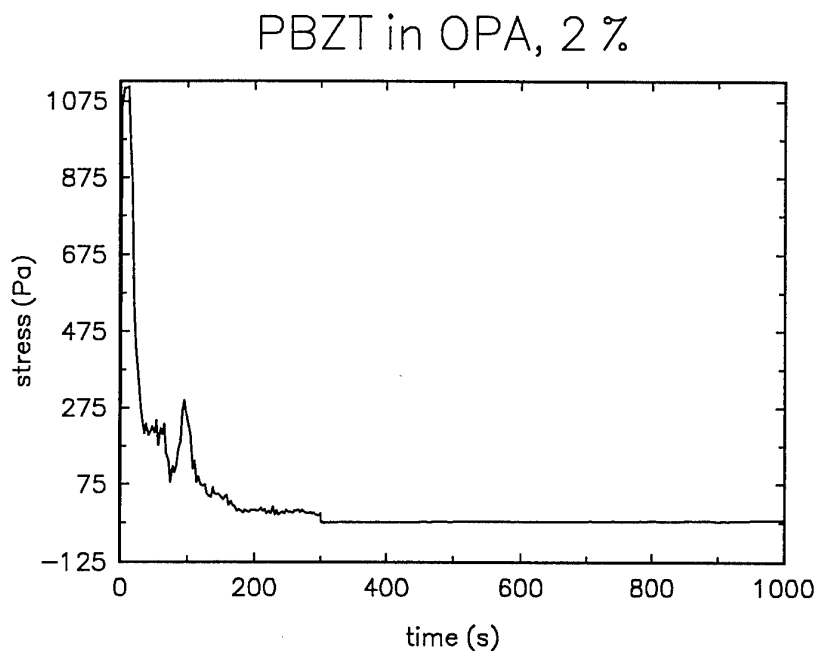


Figure 5: Shear and relaxation behaviour of a 2 % solution of PBZT in OPA, 100 °C, shear rate 10 s^{-1}

The behaviour of solutions in the nematic window of the phase diagram is very different (Figure 6). In principle the following has been observed. A very small shear rate (0.1 s^{-1}) causes a build up in stress until a plateau is reached. The relaxation behaviour is similar to that described previously (Heberer and Odell). With increase in shear rate, the plateau is reached in a shorter time, the initial overshoot becoming higher.

The investigation of the upper phase transition (peritectic line, transition from region A to B) into the region of the crystal solvate 4 and the isotropic liquid (solvent) were performed on a 9 % solution in OPA. Figure 6 shows the curves for transient experiments at different temperatures.

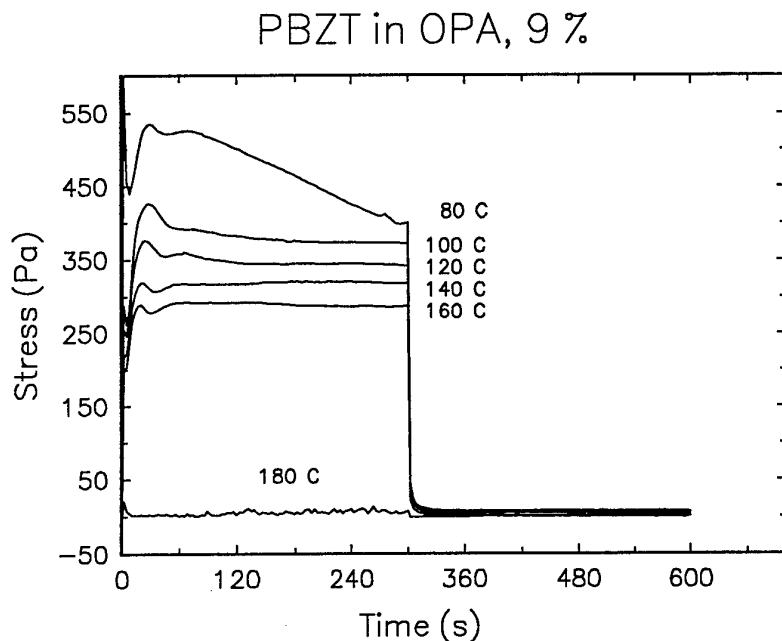


Figure 6: Shear and relaxation behaviour of a 9 % solution of PBZT in OPA at different temperatures, shear rate 3 s^{-1}

With increase in temperature the plateau of stress decreases due to the decrease of the viscosity of the nematic solution with temperature. A sudden change occurs after crossing the phase transition line at about $180 \text{ }^\circ\text{C}$. The transition line should not be affected by shear because it is a transition forced by polycondensation of the solvent with temperature and therefore only dependent on temperature. Beyond $180 \text{ }^\circ\text{C}$ the stress drops to a very low level. The crystal solvate 4 forms a network embedded in a very low viscous liquid which acts as a lubricant. Therefore no difference is observable during or after application of shear.

Detection of the lower phase transition temperature (eutectic line, region A to C) and of the left hand side of the phase diagram (chimney, region A to D and to E) was possible due to a different effect. Following cessation of shear from high shear rates, nematic solutions showed an initial fast process

of stress relaxation followed by a build up in stress with time to the level during shear. This was found not only in the nematic range of the system PBZT-OPA-Water but also in the nematic region of the system Hydroxypropylcellulose (HPC)-Water. The stress recovery is a function of temperature, molecular weight and concentration. Although the origin of this effect is not completely clear, the appearance of stress recovery was a good indication for the nematic state. Figure 7 shows the differences in the relaxation while crossing the dividing line between region C and A.

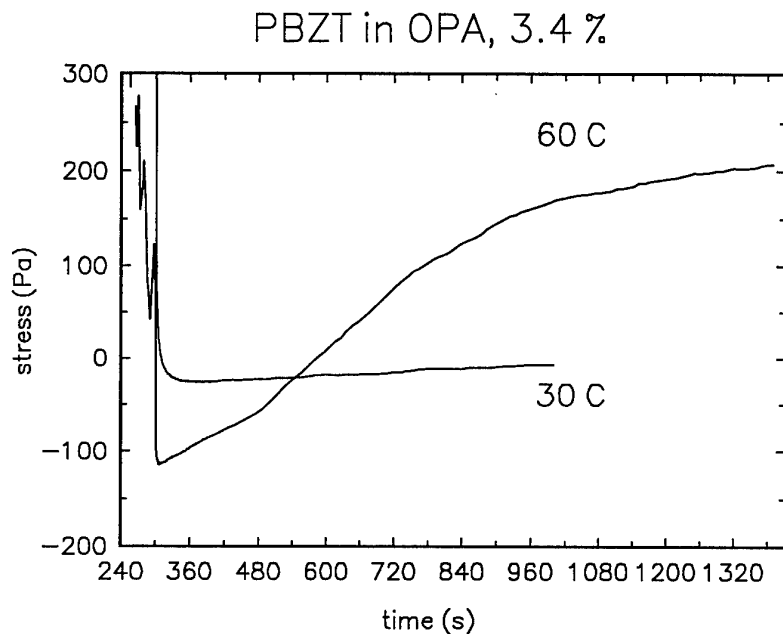


Figure 7: Shear and relaxation behaviour of a 3.4 % solution of PBZT in OPA at 30 °C and at 60 °C, shear rate 10 s⁻¹

Although the 3.4 % PBZT solution shows at 60 °C the previously described stress recovery behaviour of nematic solutions, the sample at 30 °C remains still in the biphasic region C crystal/ nematic. This transition line should also not be effected by the application of shear since the stress will not be applied

to the solid particles and therefore the melting temperature will not be affected. The mixture behaves similar to the above described biphasic mixture crystal solvate 4/ isotropic liquid. Also here, a solid and a liquid phase is mixed, and therefore the relaxation behaviour effected from the separation of the two phases. Similar behaviour was detected for the transition through the chimney crossing the dividing lines between region A and E and between region E and D. The Figures 8 and 9 show the observed relaxation behaviour for solutions of 3.4 % and 4.6 %.

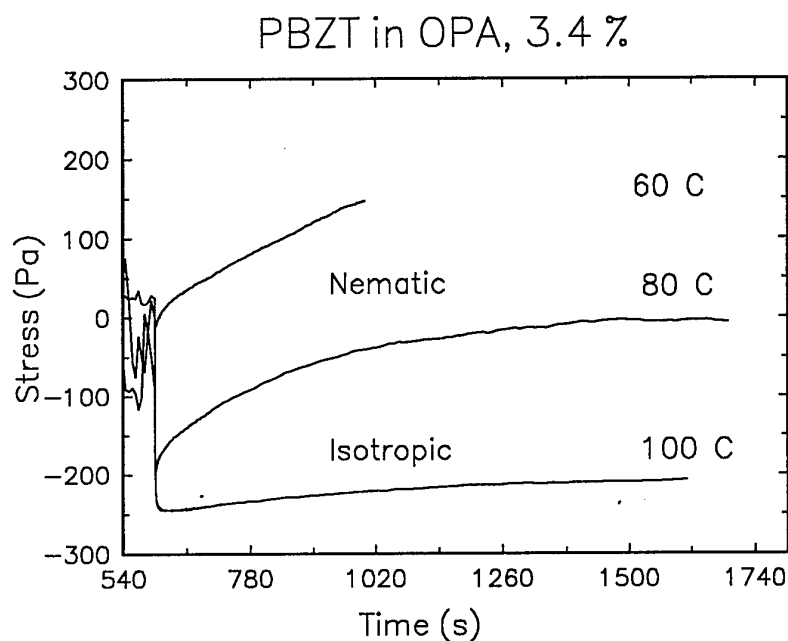


Figure 8: Shear and relaxation behaviour of a 3.4 % solution of PBZT in OPA at 60 °C, 80 ° and at 100 °C, shear rate 10 s⁻¹

Figure 8 shows the same solution (3.4 %) at higher temperatures illustrating that the stress recovery is lost as we move from the nematic into the isotropic phase (> 100 °C). Figure 9 shows the stress recovery for a higher concentration (4.6 %).

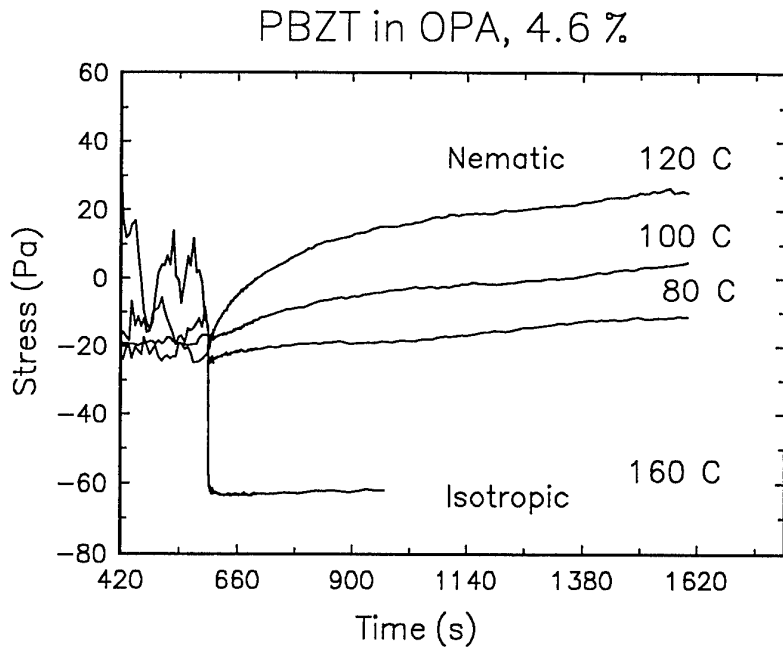


Figure 9: Shear and relaxation behaviour of a 4.6 % solution of PBZT in OPA at 80 °C, 100 °C, 120 °C and at 140 °C, shear rate 10 s^{-1}

Again very different relaxation behaviour is formed in the two regions of the phase diagram, nematic/nematic biphasic and isotropic is observable. The nematic solutions all show a shear recovery, which does increase with an increase in temperature due to the decrease in viscosity with temperature. After crossing the phase transition line towards the isotropic phase shear recovery is no longer detectable.

To summarize, the shear experiments confirm the phase diagram of the system PBZT-OPA/DPA-Water as described previously. Only small effects of shear upon the position of lines of phase transitions has been noticed. These are illustrated by the dotted lines in Figure 4 and were estimated from the previously described experiments with the 3.4 % and 4.6 % solutions. The nematic state shows a remarkable shear recovery behaviour after application of moderate shear rates.

CONCLUSIONS

The principal conclusions of this work are the following:

1. We have measured the viscosities of PBZT solutions and PPA solvents over a wide variety of concentrations, temperature and shear rate.
2. The rheology, as expected for a liquid-crystalline polymeric material is complex, and is strongly related to the PBZT-PPA-Water phase diagram.
3. The isotropic solution show a relatively high viscosity and strong shear thinning.
4. In the nematic state we observe a remarkable stress recovery after cessation of shear.
5. For initially nematic solutions the stress recovery gradually disappears as we approach the isotropic phase.
6. The presence of crystal solvate 4 dramatically reduces the solution viscosity.
7. The shear appears to have a relatively small but clear effect on the phase diagram, pushing the isotropic-nematic transition towards lower concentration.

REFERENCES

Fischer, Odell, Murray and Keller, *J.Mater.Sci.*, in press and previous ERO/AFO reports

Heberer and Odell, *J. Mater.Sci.*, in press and previous ERO/AFO reports