Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

A relationship between dielectric permittivity of the nematic continuous phase material and the shear stresses of electro-rheological fluids containing liquid crystalline materials

Christopher Malins[a]; David Lacey[a]
[a] School of Chemistry, The University of Hull, Hull, UK

To cite this Article Malins, Christopher and Lacey, David(1996) 'A relationship between dielectric permittivity of the nematic continuous phase material and the shear stresses of electro-rheological fluids containing liquid crystalline materials', Liquid Crystals, 20: 5, 517 — 525
To link to this Article: DOI: 10.1080/02678299608031138
URL: http://dx.doi.org/10.1080/02678299608031138

LIQUID CRYSTALS, 1996, VOL. 20, NO. 5, 517-525

A relationship between dielectric permittivity of the nematic continuous phase material and the shear stresses of electro-rheological fluids containing liquid crystalline materials

by CHRISTOPHER MALINS and DAVID LACEY*
School of Chemistry, The University of Hull, Hull, HU6 7RX, UK

(Received 5 September 1995; in final form 30 November 1995; accepted 20 December 1995)

Further investigations into the behaviour of electro-rheological fluids containing liquid crystalline materials have been made. Dramatic changes in the shear stresses of such suspensions have been observed around the temperature at which the liquid crystalline component undergoes a change of phase from the nematic to the isotropic phase. The temperature profile of shear stress is predicted to be mirrored by that of the mean dielectric permittivity of the liquid crystalline component in the electro-rheological fluid.

1. Introduction

The use of liquid crystalline materials as the continuous fluid phase in electro-rheological fluids (ERFs) is a relatively novel and interesting area of electro-rheological (ER) research. The traditional view of an ERF is that of finely divided dielectric solid or polymer particles (the dispersed phase) suspended in an insulating oil (the continuous phase). On the application of an electric field perpendicular to the direction of flow, the rheology of these suspensions will change from that of a normal Newtonian fluid to that of a non-Newtonian (Bingham) body. Such changes in rheology are reversible (although subject to hysteresis) on the discontinuation of the electric field and occur in milliseconds, resulting in ERFs with shear stresses of typically 3-4 kPa for an electric field strength of $\sim 2\,\mathrm{kV\,mm^{-1}}$. The ER effect has been well studied in recent years and has been found to be proportional to electric field strength for a given fluid system [1]. More complex relationships have been shown to exist between shear stress and the physical characteristics of the materials which constitute the ERF. Further discussion of such relationships can be found elsewhere [2].

Thermotropic liquid crystals are a unique class of materials in that they exhibit self-organizing phases called *mesophases* [3-6] on the application of heat. These phases are both fluid and structured, going from the very viscous and highly structured crystal and smectic phases to the more liquid-like and less ordered nematic and chiral nematic phases. The peculiar physical properties of these materials therefore make their inclusion in ERFs an interesting area of investigation. Most of the physical properties of liquid crystalline materials are anisotropic in nature, for example, possessing two dielectric permittivities, parallel and perpendicular to the director [7]. Unusual properties such as this, coupled with the morphological behaviour intrinsic to liquid crystalline materials, could affect the shear stresses of ER fluids incorporating such materials in a variety of interesting ways.

The ER effect is thought to be a result of the organization of electrostatically induced dipolar particles of the dispersed phase of the ERF into field-induced microstructures (chains or clusters) between two electrodes [8]. The strength of such associations has been shown to be related to the dielectric behaviour of the constituents of the ER fluid [2]. The dielectric permittivity can be significantly altered in a range of structurally similar materials [9] possessing the same molecular core by the careful selection of different terminating functional groups of varying polarity. These materials can then be incorporated into a liquid crystalline continuous phase. Such changes are not easily achieved for conventional continuous phase materials, and so this could lead to the greater understanding of the relationship between shear stress and dielectric permittivity in such systems.

2. Experimental

Measurement of the shear stress of an ERF was undertaken using a laminar flow shear cell, which we constructed for this purpose. All experiments were carried out in an environment thermostatically controlled by an RS 340-083 heat controller. Compensation for heat lost to the surroundings was made using a suitable calibration procedure [10]. All temperatures shown (°C) are correct to ±2·2% over the whole temperature range.

---

*Author for correspondence.

0267-8292/96 $12·00 © 1996 Taylor & Francis Ltd.

A voltage ranging from 0·2 to 2·2 kV mm^{-1} d.c. was applied across the two electrodes of the ER test apparatus using a Wier Electronics Maxireg 761 voltage supply and a Kepco 0–5 000 V voltage amplifier. Measurements of shear stress of the ERF, whilst exposed to the electric field, were taken using a Eurisem Techniks digital force gauge, which measured a value for the maximum weight applied to achieve significant flow in the ERF. The electric field was applied perpendicular to the direction of the applied stress field. From these values, the shear stresses for the electro-rheological fluids were calculated. Error assessment carried out on the apparatus used can be found elsewhere [10]. Shear stress data presented here were found to be correct to ±6·6%. It is important to emphasize that the method used in this study to determine the shear stress does not give an absolute value, as zero shear rate is assumed using this static method of measurement. However, the method is a useful technique for comparing the shear stresses of electro-rheological fluids.

Values for dielectric permittivities of liquid crystalline mixtures were obtained by capacitive measurements of the electrical deformation of the material in question, homogeneously aligned in a non-twist liquid crystal cell. The alignment of the liquid crystalline material was achieved by obliquely evaporating SiO_x onto the glass supporting surfaces of the cell of active area 1 cm^2 in a thermostatically controlled environment. The cell capacitance was measured on a HP 4284 A LCR meter (20 Hz–1 MHz) and data handling was performed on an IBM PC.

Unless indicated otherwise, thin layer chromatography was performed using an eluant of 2 : 1 (dichloromethane: petroleum fraction bp 60–80°C), and HPLC was carried out on a reverse phase column (25 x 0·46 cm C18 Microsorb Dynamax column, 5 mm pore size) eluting with acetonitrile. Infrared (IR) spectra were obtained using a Perkin Elmer 580B spectrometer. KCl or KBr discs were used for crystalline compounds and films between KBr discs were used for liquids. ^{1}H nuclear magnetic resonance (^{1}H NMR) spectra were obtained using a JMN GX270 FT spectrometer. Deuteriated chloroform was used as solvent and tetramethylsilane as the internal standard. The multiplicities of absorptions are denoted by singlet (s), doublet (d), triplet (t), quartet (q) and multiplet (m). Mass spectra (MS) were obtained on a Finnigan MAT 1020 GC/MS spectrometer; M$^+$ represents the molecular ion.

3. Synthesis of compounds

3.1. *Tetrakis(triphenylphosphine)palladium(0)*

A stirred suspension of palladium chloride (1·0 g, 6·0 mmol), triphenylphosphine (7·4 g, 0·03 mol) and dimethylsulphoxide (70 ml), under an atmosphere of dry nitrogen, was heated (60°C) until complete solution of the components occurred. Stirring was then continued in the absence of heat for a further 15 min before hydrazine hydrate (1·2 g, 0·024 mol) was added dropwise. The reaction mixture was immediately cooled to room temperature and crystals of crude product were filtered off under dry nitrogen, and washed with water (200 ml), ethanol (100 ml) and diethyl ether (100 ml) before drying over dry nitrogen for 24 h. Yield = 6·5 g (94%). No conformational analysis was undertaken on the product as degradation takes place rapidly in the presence of oxygen. The sample was stored in the dark and under an atmosphere of dry nitrogen.

3.2. *1-Bromo-4-pentoxyphenol (1)*

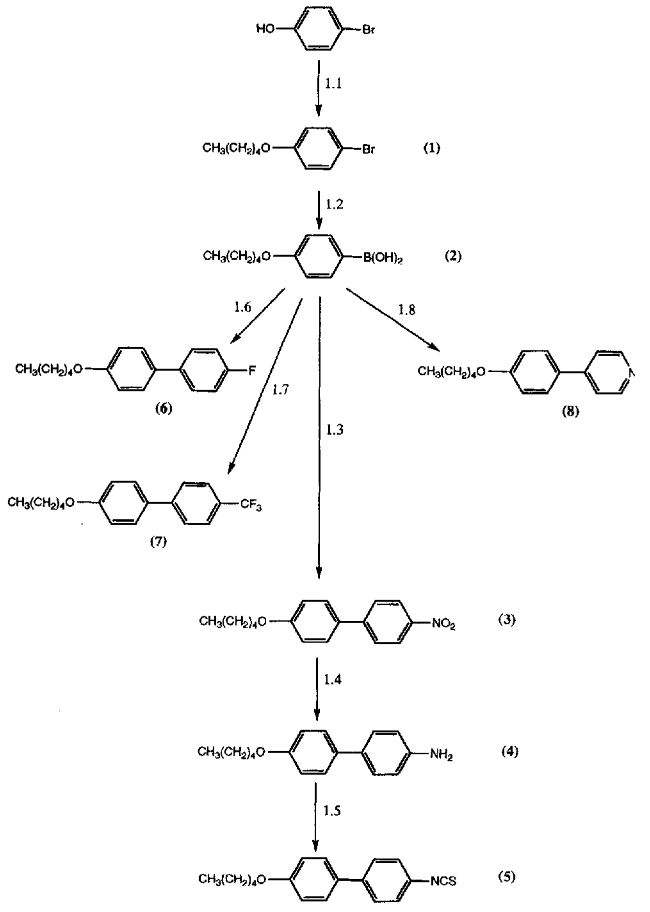
This compound, together with compounds (**2**–**8**) was prepared using scheme 1. 1-Bromopentane (14·3 g, 0·095 mol) was added to a stirred suspension of 4-bromophenol (16·4 g, 0·095 mol), anhydrous potassium carbonate (13·8 g, 0·1 mol) and potassium iodide (few mg) in dry *N*,*N*-dimethylformamide (150 ml). The resulting mixture was stirred and heated under reflux with the exclusion of moisture for 24 h. The reaction mixture was then poured into water (500 ml), the crude product extracted into diethyl ether (2 x 300 ml) and the combined organic extracts washed with water (500 ml) and dried ($MgSO_4$). The solvent was then removed to yield a yellow oil. Yield = 16·0 g (70%). The purity of the product was checked by TLC (silica gel, single spot).

IR ν_{max}/cm^{-1} 2980, 2940, 2880, 2840, 1590, 1580, 1490, 1470, 1440, 1380, 1250, 1170, 1100, 1070, 1000, 820. ^{1}H NMR δ: 0·9(3H, t, CH_3), 1·2–1·7(6H, m, 3 x CH_2), 3·9(2H, t, CH_2O), 6·8(2H, d, arom), 7·3(2H, d, arom).

3.3. *4-Pentoxyphenylboronic acid (2)*

Butyllithium (2·5 M solution in hexane; 30 ml, 0·075 mol) was added dropwise to a stirred solution of 1-bromo-4-pentoxyphenol (16·0 g, 0·066 mol) in dry tetrahydrofuran (60 ml) at −78°C under dry nitrogen. After stirring for 2·5 h a cooled solution (−5°C) of triisopropyl borate (20·0 g, 0·096 mol) in dry tetrahydrofuran (30 ml) was added dropwise and the reaction mixture was then allowed to reach room temperature overnight. Hydrochloric acid (10% v/v, 200 ml) was added to the mixture which was stirred for 1 h. The crude product was extracted into diethyl ether (2 x 200 ml) and the combined organic extracts were washed with water (500 ml) and dried ($MgSO_4$). Solvent was then removed *in vacuo* and the crude material was recrystallized (dichloromethane) to yield white needles. Yield = 13·1 g (95%). The purity of the product was checked by TLC (silica gel, single spot).

IR ν_{max}/cm^{-1} 3400, 2980, 2940, 2880, 1610, 1570, 1510, 1490, 1470, 1460, 1410, 1370, 1350, 1290, 1250, 1180,



1.1 K_2CO_3, KI, $CH_3(CH_2)_4Br$.
1.2 (i) *n*-butyllithium, THF, -78°C; (ii) $B(OCH(CH_3)_2)_3$,THF; (iii) HCl.
1.3 K_2CO_3, 1-bromo-4-nitrobenzene, Pd catalyst.
1.4 (i) Fe, HCl, EtOH; (ii) K_2CO_3; (iii) NH_4OH.
1.5 (i) CS_2, $N(Et)_3$, (ii) ethyl chloroformate, $N(Et)_3$; (iii) HCl.
1.6 K_2CO_3, 1-bromo-4-flurorobenzene, Pd catalyst.
1.7 K_2CO_3, 1-bromo-4-trifluroromethylbenzene, Pd catalyst.
1.8 K_2CO_3, 4-bromopyridine hydrochloride, Pd catalyst.
Pd catalyst=tetrakis(triphenylphosphine)palladium(0).

Scheme 1

1120, 1020, 820. ^{1}H NMR δ: 0·9(3H, t, CH_3), 1·2–1·7(6H, m, 3 x CH_2), 3·9(2H, t, CH_2O), 6·8(2H, d, arom), 7·3(2H, m, arom), 7·8(2H, s, OH).

3.4. *4'-Nitro-4-pentoxybiphenyl (3)*

A solution of 4-pentoxyphenylboronic acid (5·1 g, 0·024 mol) in dimethoxyethane (30 ml) was added dropwise to a stirred mixture of 1-bromo-4-nitrobenzene (4·9 g, 0·025 mol), tetrakis(triphenylphosphine) palladium(0) (0·99 g, 0·8 mmol) and aqueous potassium carbonate (2 M solution; 25 ml, 0·055 mol) in dimethoxyethane (40 ml). The mixture was heated under reflux under a dry nitrogen atmosphere. After 24 h the crude product was extracted into diethyl ether (2 x 200 ml), washed with brine (500 ml) and dried ($MgSO_4$). The crude material was then purified by column chromatography (petroleum fraction bp 60–80°C: dichloromethane, 3 : 1) and recrystallized (methanol) to yield yellow crystals. Yield = 3·5 g (51%); mp 54·2–54·4°C. The purity of the product was checked by TLC (silica gel, single spot) and HPLC (99·0%).

MS (*m/z*) 285 (M +), 215, 185, 171, 139. IR ν_{max}/cm^{-1} 3100, 2960, 2940, 2870, 2850, 1600, 1580, 1510, 1490, 1470, 1380, 1340, 1300, 1250, 1200, 1110, 1010, 860, 840, 750. ^{1}H NMR δ: 0·9(3H, t, CH_3), 1·5–1·7(6H, m, 3 x CH_2), 4·0(2H, t, CH_2O), 7·0(2H, d, arom), 7·6(4H, m, arom), 8·3(2H, m, arom).

3.5. *4'-Amino-4-pentoxybiphenyl (4)*

A stirred suspension of 4'-nitro-4-pentoxybiphenyl (2·7 g, 9·5 mmol), iron pin dust (1·8 g, 0·035 mol) and hydrochloric acid (36 M aqueous solution; 1·5 ml, 0·045 mol) in ethanol (40 ml) was heated under reflux for 18 h. Anhydrous potassium carbonate (0·95 g, 7·0 mmol) was added and stirring was continued for a further 30 min before an excess of aqueous ammonia was added. The resultant precipitate of ferric oxide was filtered off and washed with hot ethanol (20 ml). The filtrate was treated with diethyl ether (2 x 200 ml) and the combined organic extracts were washed with water (500 ml) and dried ($MgSO_4$). Solvent was then removed *in vacuo* and the crude product was recrystallized (petroleum fraction bp 60–80°C: dichloromethane, 3 : 1) to yield an off-white powder. Yield = 2·1 g (76%); mp 126–127°C. The purity of the product was checked by TLC (silica gel, single spot) and HPLC (100%).

MS (*m/z*) 257 (M +), 229, 211, 184, 171, 156. No other conformational analysis was undertaken due to the carcinogenic nature of the product.

3.6. *4'-Isothiocyanyl-4-pentoxybiphenyl (5)*

Carbon disulphide (1·1 ml) and triethylamine (2·2 ml) were added to a stirred solution of 4'-amino-4-pentoxybiphenyl (3·5 g, 0·0136 mol) in a mixture of benzene (32 ml) and hexane (8 ml). The reaction mixture was left to stand at 0°C for 48 h after which time the yellow triethylammonium dithiocarbonate salt was filtered off, washed with hexane (20 ml) and dried *in vacuo*. The salt was then redissolved into a mixture of chloroform (35 ml) and triethylamine (5 ml) and the solution cooled (0°C) before ethyl chloroformate (5 ml) was added with stirring. The solution was allowed to warm to room temperature with continued stirring for 1 h and then poured into hydrochloric acid (10% v/v, 200 ml). The organic layer was separated off, washed with water (100 ml) and dried ($MgSO_4$). The solvent was then removed *in vacuo*. The crude material was purified by column chromatography (petroleum fraction b.p. 60–80°C: dichloromethane, 1 : 1) and the product recrystallized (methanol) to yield yellow crystals. Yield = 0·8 g (20%); mp 112·2–112·4°C. The purity of the product was checked by TLC (silica gel, single spot) and HPLC (99·4%).

MS (*m*/*z*) 297 (M +), 227, 198, 151, 58, 43. IR ν_{max}/cm^{-1} 2960, 2940, 2870, 2860, 2020, 1610, 1580, 1490, 1480, 1470, 1380, 1290, 1250, 1190, 1110, 1100, 1010, 820. ^{1}H NMR δ: 0·9(3H, t, CH_3), 1·4–1·7(6H, m, 3 x CH_2), 4·0(2H, t, CH_2O), 6·9(2H, d, arom), 7·3(2H, m, arom), 7·6(4H, m, arom).

3.7. *4′-Fluoro-4-pentoxybiphenyl (6)*

The reaction was carried out using a similar procedure to that described for the preparation of compound **3**; quantities used were 4-pentoxyphenylboronic acid (3·0 g, 0·014 mol) in dimethoxyethane (10 ml), 1-bromo-4-fluorobenzene (2·2 g, 0·0125 mol), tetrakis(triphenylphosphine)palladium(0) (0·49 g, 0·42 mmol) and aqueous potassium carbonate (2 M solution; 18 ml, 0·036 mol) in dimethoxyethane (25 ml). After removal of the solvent the crude material was purified by column chromatography [petroleum fraction bp 60–80°C: dichloromethane, 3 : 1] and the product recrystallized (methanol) to yield white crystals. Yield = 0·96 g (33%); mp 82·0–83·0°C. The purity of the product was checked by TLC (silica gel, single spot) and HPLC (99·7%).

MS (*m*/*z*) 258 (M +), 188, 169, 159, 133. IR ν_{max}/cm^{-1} 3100, 2950, 2940, 2880, 1610, 1570, 1500, 1470, 1460, 1390, 1290, 1250, 1190, 1160, 1010, 830. ^{1}H NMR δ: 0·9(3H, t, CH_3), 1·4–1·8(6H, m, 3 x CH_2), 4·0(2H, t, CH_2O), 7·0(2H, d, arom), 7·1(2H, m, arom), 7·3(2H, m, arom), 7·5(2H, m, arom).

3.8. *4-Pentoxy-4′-trifluoromethylbiphenyl (7)*

The reaction was carried out using a similar procedure to that described for the preparation of compound **3**; quantities used were 4-pentoxyphenylboronic acid (1·0 g, 4·8 mmol) in dimethoxyethane (20 ml), 1-bromo-4-trifluoromethylbenzene (1·0 g, 4·4 mmol), tetrakis(triphenylphosphine)palladium(0) (0·18 g, 0·15 mmol) and aqueous potassium carbonate (2 M solution; 6 ml, 0·012 mol) in dimethoxyethane (10 ml). After removal of the solvent the crude material was purified by column chromatography (petroleum fraction bp 60–80°C: dichloromethane, 3 : 1) and the product recrystallized (petroleum fraction bp 60–80°C) to yield white crystals. Yield = 0·6 g (45%); mp 122·0–123·0°C. The purity of the product was checked by TLC (silica gel, single spot) and HPLC (98·8%).

MS (*m*/*z*) 308 (M +), 238, 209, 183. IR ν_{max}cm^{-1} 3080, 2960, 2940, 2880, 1600, 1580, 1500, 1470, 1440, 1300, 1250, 1170, 1130, 1010, 830, 750. ^{1}H NMR δ: 0·9(3H, t, CH_3), 1·4–1·8(6H, m, 3 x CH_2), 4·0(2H, t, CH_2O), 7·0(2H, d, arom), 7·3(2H, m, arom), 7·5(2H, m, arom), 7·6(2H, m, arom).

3.9. *4-(4-Pentoxy)phenylpyridine (8)*

The reaction was carried out using a similar procedure to that described for the preparation of compound **3**: quantities used were 4-pentoxyphenylboronic acid (2·0 g, 0·01 mol) in dimethoxyethane (20 ml), 4-bromopyridine hydrochloride (1·9 g, 9·0 mmol), tetrakis(triphenylphosphine)palladium(0) (0·38 g, 0·3 mmol) and aqueous potassium carbonate (2 M solution; 16 ml, 0·032 mol) in dimethoxyethane (30 ml). After removal of the solvent the crude material was purified by column chromatography (methanol) and the product was recrystallized (petroleum fraction bp 60–80°C) to yield brown crystals. Yield = 0·46 g (23%): mp 47·0–48·0°C. The purity of the product was checked by TLC (silica gel, acetone, single spot) and HPLC (96·4%).

MS (*m*/*z*) 241 (M +), 171, 115, 89, 77. IR ν_{max}/cm^{-1} 3080, 3040, 2960, 2940, 2870, 1610, 1600, 1580, 1560, 1520, 1490, 1470, 1450, 1290, 1250, 1220, 1180, 1120, 1090, 1070, 1030, 1010, 830, 820. ^{1}H NMR δ: 0·9(3H, t, CH_3), 1·4–1·8(6H, m, 3 x CH_2), 4·0(2H, t, CH_2O), 7·3(4H, q, arom), 7·5(2H, m, arom), 8·6(2H, q, arom).

3.10. *4,4′-Dipentoxybiphenyl (9)*

This compound was prepared using scheme 2. 1-Bromopentane (3·0 g, 0·02 mol) was added to a stirred suspension of 4,4′-dihydroxybiphenyl (2·0 g, 0·01 mol), anhydrous potassium carbonate (3·2 g, 0·022 mol) and potassium iodide (few mg) in dry *N*,*N*-dimethylformamide (50 ml). The resulting mixture was stirred and heated under reflux with the exclusion of moisture for 24 h. The reaction mixture was then poured into water (250 ml) and the crude product was extracted into diethyl ether (2 x 200 ml). The combined organic extracts were washed with water (500 ml) and dried ($MgSO_4$). The solvent was then removed *in vacuo* and the product was purified by column chromatography (petroleum fraction bp 60–80°C: dichloromethane, 1 : 1) and recrystallized (acetone) to yield colourless plates. Yield = 0·86 g (26%). The purity of the product was checked by TLC (silica gel, single spot) and HPLC (100%).

MS (*m*/*z*) 326 (M +), 256, 186, 157. IR ν_{max}/cm^{-1} 2960, 2940, 2870, 2860, 1610, 1570, 1500, 1480, 1470, 1260, 1250, 1180, 1140, 1040, 830. ^{1}H NMR δ: 0·9(6H,

2.1. K_2CO_3, KI, $CH_3(CH_2)_4Br$

Scheme 2

t, CH_3), 1·4–1·7(12H, m, 6 x CH_2), 3·9(4H, m, CH_2O), 6·9(4H, m, arom), 7·5(4H, m, arom).

All other materials were obtained from Merck Ltd. (Poole) or commercially purchased. Nematic liquid crystal mixture E7[11] and the single component liquid crystal materials, K21, K24, M9, M15, T15 and I52 were kindly donated by Merck Ltd. (Poole). Lithium poly(methacrylate)—Lipma (moisture content 15 wt% determined by DTA analysis)—was obtained from Advanced Fluid Systems (London), and Cereclor 50LV was supplied by ICI Chemicals.

4. Results and discussion

In previous studies [12–13], ER fluids consisting of lithium poly(methacrylate) as the dispersed phase and either E7 or Cereclor 50LV as the continuous phase have shown substantial ER activity. In this study we will highlight some of the behavioural characteristics shown by ER fluids incorporating liquid crystalline materials. It has been shown that increasing the volume or weight fraction of the dispersed phase causes an increase in shear stress for many ER fluids [8, 14]. Increasing the weight fraction increases the number of colloidal aggregates per unit volume in the dispersion. These aggregates are thought to be responsible for the resistance to flow observed in ER fluids. Using Lipma as the dispersed phase the behaviour of the shear stresses of the ER fluids containing E7 (a nematic liquid crystalline mixture) and Cereclor 50 LV with increasing temperature was investigated. Mixtures of between 10–40 wt% lithium poly(methacrylate) dispersed in E7 or Cereclor 50LV were examined for ER activity over a temperature range of 20–80°C. The results from this part of our study are given in figures 1 and 2.

From figure 1, a plot of shear stress against temperature for weight fractions of 0·1 to 0·4 of the dispersed phase Lipma with Cereclor 50LV as the continuous phase, the thermal profile of the shear stresses for all of the ER fluids examined here is shown to be very similar. An initial rise in the shear stress is observed with increasing temperature to a maximum shown in the region of 30 to 50°C. This maximum appears to be influenced by the weight fraction (ϕ) of the dispersed phase contained in the fluid. On increasing ϕ the temperature at which a maximum shear stress is observed is seen to decrease, from 50°C at $\phi = 0·1$ to 35°C at $\phi = 0·4$. This is then followed by a decrease in the shear stress. As expected, we observed a general increase in shear stress as the volume fraction ϕ of the dispersed phase was increased. This is characteristic behaviour for ER fluids and the reasons for this are discussed elsewhere [14–16].

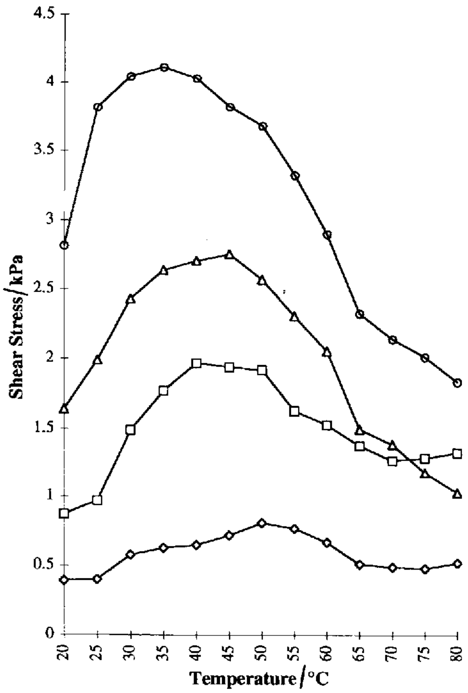


Figure 1. Plot of shear stress against temperature for ER fluids containing Lipma and Cereclor 50LV at a voltage stress of 2·20 kVmm^{-1}. ◇ 10% Lipma, 90% Cereclor 50LV; □ 20% Lipma, 80% Cereclor 50LV; △ 30% Lipma, 70% Cereclor 50LV; ○ 40% Lipma, 60% Cereclor 50LV.

This rapid decrease in the shear stresses of ER fluids incorporating the continuous phase Cereclor 50LV at a temperature around 50 to 60°C was also shown for those ER fluids containing E7 (see figure 2). What was significantly different was that the suspensions containing E7 showed a definite temperature at which a maximum value for the shear stress was achieved. For all weight fractions of the dispersed phase with a continuous phase of E7, the maximum shear stress was found at a temperature of 50°C, which is fairly close to the nematic to isotropic phase transition of the liquid crystalline component of the ER fluid and equivalent to a reduced temperature of $0·97T_{N-I}$, the value used for all of the E7 mixtures in this study.

It would be slightly premature to associate this behaviour only with the physical properties of the continuous phase material, as the behaviour of the dispersed phase has also to be considered. Lipma is a hydrous polymer and contains around 15% water. The amount of water present in the polymer has been shown to have a significant influence on the shear stresses of dispersions in which it is employed [17, 18]. In an open system, as used here, when heated to a sufficiently high temperature, the moisture contained within the dispersed phase particulates of Lipma will gradually evaporate. As a result of this, the shear stresses of suspensions containing Lipma will be affected and their shear stresses will decrease

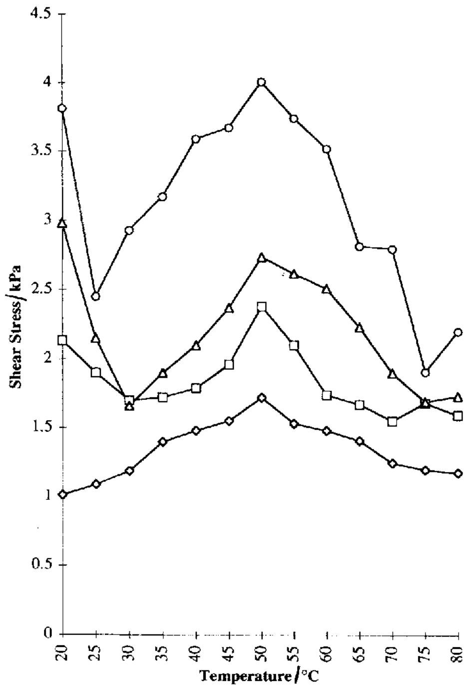


Figure 2. Plot of shear stress against temperature for ER fluids containing Lipma and E7 at a voltage stress of $2{\cdot}20\,\mathrm{kV\,mm^{-1}}$. ◇ 10% Lipma, 90% E7; □ 20% Lipma, 80% E7; △ 30% Lipma, 70% E7; ○ 40% Lipma, 60% E7.

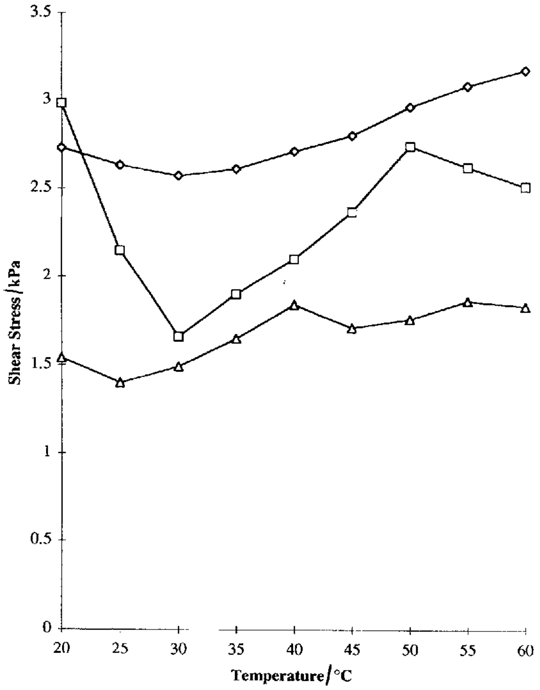


Figure 3. Plot of shear stress against temperature for ER fluids containing 30% Lipma and (a) 70% E7 □; (b) 25% K21, 25% K24, 10% M9 and 10% T15 (Mixture B) ◇; (c) 30% K21, 30% K24 and 10% M9 (Mixture A) △. All at a voltage stress of $2{\cdot}20\,\mathrm{kV\,mm^{-1}}$.

rapidly when this loss of moisture occurs. Such a rapid decrease is observed for suspensions of E7 and Cereclor 50LV with Lipma at around 60°C. This could, at least in part, be attributed to the loss of moisture from the dispersed phase at this temperature.

A further experiment was carried out to confirm that the physical properties of the continuous phase E7 were responsible for the observed maxima in the shear stresses at $0{\cdot}97T_{\mathrm{N-I}}$. Two mesomorphic mixtures were made up whose compositions were similar to that of E7, but which displayed different nematic to isotropic transition temperatures, as shown in table 1. These mixtures were used to make 3 ER fluids with Lipma and the plot of shear stress against temperature at a field strength of $2{\cdot}20\,\mathrm{kV\,mm^{-1}}$ for these suspensions are shown in figure 3. It can be seen quite clearly from the data presented in figure 3 that the nematic to isotropic transition temperature of the continuous phase mixture is of great importance to the shear stresses of ER fluids incorporating liquid crystalline materials. Mixture A, which possesses a continuous phase with a nematic to isotropic transition at 42·2°C, is seen to show a maximum shear stress at 40°C, which corresponds to $0{\cdot}99T_{\mathrm{N-I}}$ of the pure continuous phase. This figure is close to the maximum shear stresses observed for E7 which occurred at $0{\cdot}97T_{\mathrm{N-I}}$. For mixture B, whose continuous phase shows a nematic to isotropic transition at 63·8°C, the shear stress of the suspension continued to increase with temperature up to 60°C, the highest temperature used in this investigation. The temperature of 60°C corresponds to $0{\cdot}99T_{\mathrm{N-I}}$ for this continuous phase.

Table 1. Composition of the continuous phase mixtures of fluids shown in figure 3.

	Mixture composition wt %	$T_{\mathrm{N-I}}$/°C
Mixture A	42·3% K21, 42·3% K24, 14·3% M9.	42·2
Mixture B	35·7% K21, 35·7% K24, 14·3% M9, 14·3 T15.	63·8
E7	51% K15, 25% K21, 16% M24, 8% T15.	60·0

K15 = 4-cyano-4′-*n*-pentylibiphenyl, K21 = 4-cyano-4′-*n*-heptylbiphenyl, K24 = 4-cyano-4′-*n*-octylbiphenyl, M9 = 4-cyano-4′-*n*-propoxybiphenyl, M24 = 4-cyano-4′-*n*-octyloxybiphenyl, T15 = 4-cyano-4′-*n*-pentyl-*p*-terphenyl.

The most probable cause of the changes in the shear stresses of ER fluids with temperature is the dielectric behaviour of the continuous phase material, a parameter that is inextricably linked to phase behaviour in liquid crystalline materials. The dielectric permittivities of the dispersed and continuous phases have been shown to be of great importance to the shear stresses of both conventional and mesomorphic ER fluids [19, 20] and there is no reason to believe that changes in the dielectric permittivity of the base fluid with increasing temperature would not have a pronounced effect on the shear stress of the suspension. The dielectric permittivity of Cereclor 50LV has a simple temperature dependence, rising slowly with increasing temperature until the decomposition point of the oil (around 140°C) is reached. This increase can therefore be associated with the increases in shear stress seen in this study with temperature for dispersions containing Cereclor 50LV. The temperature dependence of the permittivity of liquid crystalline materials is more complex and has been discussed elsewhere [21, 22]. A basic relationship between the dielectric anisotropy of the continuous phase and the shear stress of the ER fluid has been described previously [10], but perhaps a more meaningful relationship exists between the shear stress of the ER fluid and the mean permittivity, $\bar{\varepsilon}$, of the continuous phase, since the exact mechanism by which the LC ER fluid operates is not known and therefore it is difficult to predict, with certainty, the contributions of $\varepsilon\|$ and $\varepsilon\perp$ to the overall ER effect. The mean permittivity value takes into account both $\varepsilon\|$ and $\varepsilon\perp$ and therefore it is better at this stage to use $\bar{\varepsilon}$ to reflect the contribution of the dielectric properties of the liquid crystalline phase to the ER effect exhibited by the LCER fluids. The mean permittivities of the liquid crystalline materials are calculated from equation (1) by measuring both the dielectric permittivities $\varepsilon\|$ and $\varepsilon\perp$. The method used to measure $\varepsilon\|$ and $\varepsilon\perp$ is described in the experimental section and uses a cell with homogeneous alignment. This type of alignment is necessary to obtain the values of $\varepsilon\|$ and $\varepsilon\perp$ from the data [21, 22]. In mixtures such has those used in this study which contain a large amount of dispersed particulates, it is reasonable to assume that homeotropic alignment of the liquid crystalline material in the continuous phase resulting from the applied electric field would not be uniform. The representation of the dielectric properties of the continuous phase by their mean dielectric permittivities gave excellent correlation with the shear stresses of the ER fluids at different temperatures, as will be shown later. This behaviour is characterized by a rise in $\bar{\varepsilon}$ as the temperature of the ER fluid is increased towards the nematic to isotropic transition. Around this point a discontinuity is observed due to certain pre-transitional effects common to nematic materials containing compounds with cyano terminal groups, which cause anti-parallel correlation of the molecules in the bulk material [23, 24].

$$\bar{\varepsilon} = (\varepsilon\| + 2\varepsilon\perp)/3 \qquad (1)$$

The highest dielectric permittivity is observed for what is called the *isotropic permittivity* ($\varepsilon_{\mathrm{iso}}$) which occurs after the nematic to isotropic transition. This is due to the retention of some nematic molecular ordering within the isotropic material. This behaviour of the dielectric permittivity of the liquid crystalline material appears to be mirrored by the shear stresses of its ER suspensions. There does appear to be a definite connection between the shear stress of a suspension and the dielectric permittivity and/or the phase behaviour of the continuous phase of the suspension as it changes with temperature.

In the results so far discussed in this study it appears that for ER fluids containing liquid crystalline materials the shear stresses of these dispersions are related strongly to the dielectric permittivity of the continuous phase material, roughly mirroring the profile of the mean permittivity with temperature. The magnitude of the shear stresses of such dispersions should therefore show some relationship to the magnitude of the mean dielectric permittivity of the continuous phase. To investigate this effect a study was undertaken to compare the shear stresses and mean dielectric permittivities of several materials when dissolved in a suitable nematic host material, keeping the size of the dopant molecule similar while changing the polarity of the terminally positioned group. For this study the materials shown in reaction schemes 1 and 2 were synthesized. One of the most important factors in this study was to keep the molecular size of the dopants about the same. By changing the polarity of the terminally positioned group, we could affect the mean permittivity of the dopant. In addition to these materials, the liquid crystalline compound M15 (4-cyano-4′-*n*-pentoxybiphenyl) was used in this study. This compound is analogous, in structure, to those shown in reaction schemes 1 and 2 and possesses a terminally positioned cyano-group.

Since some of the materials used in this study did not exhibit liquid crystalline behaviour, a host material exhibiting a wide range nematic phase and a low dielectric anisotropy had to be found in which all the materials under study were soluble. Such a material was I52 (structure given in figure 4) which has a $T_{\mathrm{N-I}}$ value of 101°C and a dielectric anisotropy of 0·03 at 20°C. For each mixture, 7·15 wt % of dopant was dissolved in the nematic host material I52. This mixture was then used as the continuous phase in dispersions containing lithium poly(methacrylate). The final composition of the ER fluid was 30% lithium poly(methacrylate), 65% I52 and 5% dopant.

The dielectric permittivity of the continuous phase (I52, dopant) was measured, and the ER activity of the

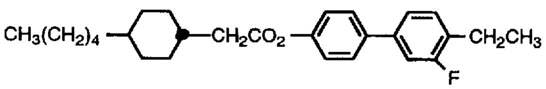


Figure 4. Structure of I52.

dispersions (I52, Lipma, dopant) was measured over a range of voltages. All of the experiments were conducted at a reduced temperature of $0{\cdot}90T_{\mathrm{N-I}}$ to ensure that all of the mixtures were at relatively the same position away from the nematic to isotropic phase transition ($T_{\mathrm{N-I}}$) to take into account the effect of the dopant on the $T_{\mathrm{N-I}}$ value of I52, the host material. The mean permittivity of liquid crystalline materials is also temperature dependent and therefore, in a study like this, it is better to examine the effect of the mean permittivity of the liquid crystalline material on the ER effect at a reduced temperature. The reduced temperatures of the mixtures are given in table 2.

A plot of the shear stresses of these dispersions against the mean dielectric permittivity of the continuous phase (I52/dopant) mixtures is shown in figure 5. This plot clearly shows a straight-line correlation between the mean dielectric permittivity of the continuous phase mixture and the shear stresses of the resultant dispersions with Lipma. This reinforces the idea that for a given dispersed phase particulate, the dielectric permittivity of the mesomorphic continuous phase does indeed have a distinct effect on the magnitude of the shear stress of the resultant dispersion.

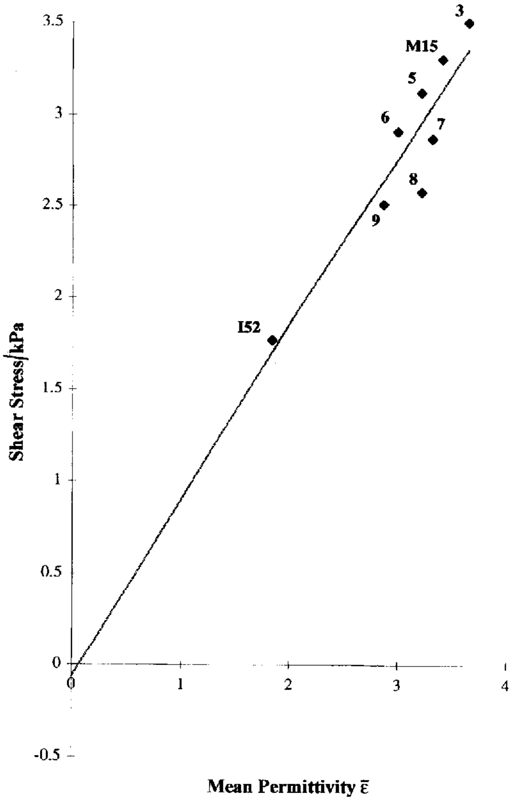


Figure 5. Plot of the shear stresses of suspensions containing a variety of dopant materials in I52 against the mean dielectric permittivity of the continuous phase mixture at $0{\cdot}90\ T_{\mathrm{N-I}}$ and $2{\cdot}20\,\mathrm{kVmm^{-1}}$.

Although the addition of a non-mesogenic material to the continuous phase would result in a disruption of the nematic phase ordering, using dopants of similar molecular size and shape should mean that such structural disruptions are occurring to the same extent in all of the ER fluids. This enables us to examine only the effect that the change in the mean dielectric permittivity has on the shear stresses of mesogenic ER fluids. By demonstrating the presence of a linear relationship between shear stress and mean dielectric permittivity, we are led to the conclusion that the temperature related behaviour of the shear stresses of ER fluids containing liquid crystalline materials can be mapped by reference to the behaviour of $\bar{\varepsilon}$ of the mesogenic component with temperature. Previously reported evidence [12] suggests a connection between the shear stress and continuous phase morphology in such systems, therefore the intrinsic relationship between the phase behaviour and the dielectric permittivity in mesogenic materials has proved to

Table 2. Data for the ER fluids comprising I52/dopant continuous phase mixtures.

Dopant	$T_{\mathrm{N-I}}/^{\circ}\mathrm{C}$	$0{\cdot}90\ T_{\mathrm{N-I}}/^{\circ}\mathrm{C}$	$\bar{\varepsilon}$	Shear stress at $2{\cdot}2\,\mathrm{kV\,mm^{-1}}/\mathrm{kPa}$
A. Host material				
I52	101·0	63·6	1·86	1·77
B. Dopants (17·5 wt %) in I52				
3	102·0	64·5	3·65	3·50
5	102·5	65·0	3·22	3·12
6	94·9	58·1	3·03	2·91
7	92·2	55·7	3·30	2·58
8	97·5	60·5	3·32	2·87
9	99·1	61·9	2·87	2·51
M15	102·3	64·8	3·42	3·30

M15 = 4-cyano-4′-*n*-pentyloxybiphenyl
Structures for dopants **3**, **5**, **6**, **7**, **8** and **9** are given in Schemes 1 or 2.
Structure of I52, see figure 4.

reinforce these observations. However, such a relationship between the shear stress and the mean permittivity of ER fluids based on liquid crystalline materials may not ultimately prove to be a simple one. We have made no attempt in this study to quantify this behaviour, and further intensive study is required to elucidate this. We do believe that, at least in part, the shear stress of an ER fluid incorporating a mesomorphic material will be dependent upon the mean permittivity and the phase behaviour of the liquid crystalline material, and by prior knowledge of such parameters, the shear stresses of ER fluids incorporating such materials could be readily predicted and perhaps controlled. Understanding this behaviour fully, therefore, could be an important step towards the attainment of a range of highly efficient and controllable ER fluids containing liquid crystalline materials.

5. Conclusions

In combination with the results shown in previous communications [12, 13], we have demonstrated that some of the intrinsic features exhibited by ER fluids containing liquid crystalline materials can be accounted for with reference to the physical properties of the liquid crystalline component. The shear stresses shown by such ERFs have proved to be dependent, in part, upon these physical characteristics. The linear relationship shown in this study between the shear stress and the mean permittivity for a range of similar materials indicates that the performance of the ER fluid is inextricably linked to the morphology and the dielectric behaviour of the liquid crystalline component. Electro-rheological fluids incorporating liquid crystalline materials have been shown to be very interesting materials, occasionally showing greater shear stresses than conventional ERFs, and perhaps ER fluids based on liquid crystalline materials can now offer an alternative 'smart fluid' in the field of ER technology.

We would like to thank Merck Ltd. (Poole) for supporting a SERC Case award for one of us (C.M.) and also for allowing us to use their dielectric equipment.

References

[1] Klass, D. L., and Martinek, T. W., 1967, *J. appl. Phys.*, **38**, 71.

[2] Conrad, H., Chen, Y., and Sprecher, A. F., 1991, in Proceedings of International Conference on ER Fluids, Carbondale, Illinois, edited by R. Tao, (London: World Scientific), p. 195.

[3] Demus, D., 1990, *Liquid Crystals Applications and Uses*, edited by B. Bahadur, (London: World Scientific) p. 1.

[4] Gray, G. W., and Goodby, J. W., 1984, *Smectic Liquid Crystals*, (Glasgow and London: Leonard Hill).

[5] Sackman, H., 1986, *Polymorphism and Plane Transition in Liquid Crystals*, (Beitrage: Martin-Luther Universtat Halle-Wittenberg Wissen Scaftl).

[6] Collings, P. J., 1990, *Liquid Crystals, Nature's Delicate Phase of Matter*, (London: Princetown Science Library).

[7] Pohl, L., 1990, *Liquid Crystals; Applications and Uses*, edited by B. Bahadur, (London: World Scientific), p. 139.

[8] Conrad H., and Sprecher, A. F., 1991, *J. Stat. Phys.*, **64**, 1073.

[9] Coates, D., 1990, *Liquid Crystals Applications and Uses*, edited by B. Bahadur, (London: World Scientific) p. 91.

[10] Malins, C., 1994, PhD thesis, University of Hull, UK.

[11] Nolan, P., Tillin, M., and Coates, D., 1992, *Mol. Cryst. liq. Cryst. Lett.*, **8**, 129.

[12] Malins, C., and Lacey, D., 1994, *Mol. Cryst. liq. Cryst.*, **4**, 1029.

[13] Hosseini-Sianaki, A., Varley, C. J., Taylor, P. M., Lacey, D., and Malins, C., *J. Mater. Chem.* (accepted for publication).

[14] Otsubo, Y., Sekine, M., and Katayama, S., 1992, *J. Rheol.*, **36**, 479.

[15] Marshall, L., Goodwin, J. W., and Zukowski, C. F., 1989, *J. Chem. Soc. Faraday Trans. I*, **85**, 2785.

[16] Klingenberg, D. J., and Zukowski, C. F., 1990, *Langmuir*, **6**, 15.

[17] Strangroom, J. E., 1983, *Phys. Technol.*, **14**, 290.

[18] Strangroom, J. E., 1980, UK Patent Application, 1570234.

[19] Evans, L. F., Harness, I., Kermode, P. R., and Strangroom, J. E., 1991, in Proceedings of International Conference on ER Fluids, Carbondale, Illinois, edited by R. Tao, (London: World Scientific) p. 154.

[20] Garino, T., Adolf, D., and Hance, B., 1991, in Proceedings of International Conference on ER Fluids, Carbondale, Illinois, edited by R. Tao, (London: World Scientific) p 167.

[21] Bradshaw, M. J., and Raynes, E. P., 1981, *Mol. Cryst. liq. Cryst.*, **72**, 73.

[22] Bradshaw, M. J., and Raynes, E. P., 1981, *Mol. Cryst. liq. Cryst.*, **72**, 35.

[23] Chandrasekhar, S., and Ratna, B. R., 1982, *Mol. Cryst. liq. Cryst.*, **82**, 193.

[24] Coles, H. J., and Sefton, M. S., 1987, *Mol. Cryst. liq. Cryst.*, **4**, 123.