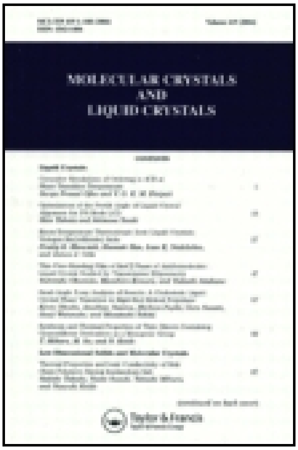

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MODIFICATION OF MAIN CHAIN LCP PROCESSABILITY AND PROPERTIES

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Abstract Spherical, fibrous and platey particulate additives have been incorporated into a thermotropic wholly aromatic polyester. The effect of additive shape and concentration on melt rheology and solid state properties has been investigated. Melt viscosity shows a greater dependence on shape than concentration. Spherical particles produce high melt viscosities. Anisotropic particles, uniaxial and biaxial, give low viscosities. Modification of moulded test shape mechanical property anisotropy, expansion coefficient anisotropy and dynamic mechanical relaxation behaviour is discussed.

INTRODUCTION

Thermotropic main chain liquid crystal polyesters, often referred to as Self Reinforcing Polymers or SRPs, are rapidly becoming established as industrially useful, high performance, engineering thermoplastics. Recognition of the processing advantages, provided by the molten mesophase, combined with useful orientation dependent solid state properties is generating widespread interest. Applications have been found in aerospace, telecommunication, electronics and transportation, for extruded fibre[1], monofilament and profiles, protective coatings on optic fibre[2-4] and precision injection mouldings.[5]

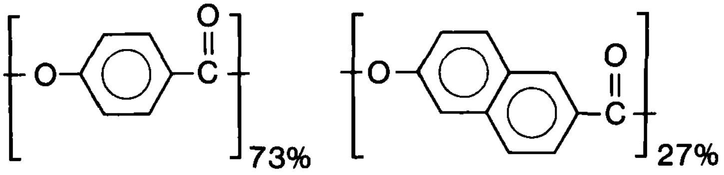
The low melt viscosity and shear thinability of the liquid crystal melt enables complicated shapes to be readily injection moulded. The melt exhibits little or no elastic response consequently die swell and warpage are small. In addition the low expansion behaviour and higher melt density compared to conventional thermoplastics results in low shrinkage and accurate mould replication. These factors, coupled with good chemical and thermal resistance, are driving the development of these polymers as precision injection moulding materials.

Orientation of SRPs by melt flow during injection moulding leads to anisotropic solid state properties. For example the anisotropy gives high strength in the injection direction put poorer mechanical properties in the transverse direction. Anisotropy can be modified using the processing conditions, mould gate design, and by the incorporation of particulate additives or fillers.

In this paper the use of particulate additives to modify main chain LCP behaviour is discussed with emphasis on the role of particle shape. Readily available spherical, platey and fibrous particles have been incorporated into a wholly aromatic LCP and the effect on melt rheology and solid state property anisotropy investigated.

EXPERIMENTAL

The main chain LCP or SRP used in this study was a wholly aromatic polyester consisting of 73 mole % p-oxybenzoyl units and 27 mole % 6-oxy-2-naphthoyl units and was prepared by a melt condensation polymerisation method[6]. The polymer was characterised by solution viscometry and had an inherent viscosity of 6.4dl/g measured on a 0.1% by weight solution in pentafluorophenol at 60°C.



The particulate additives used in the study, listed in table 1, are all readily available and are characterised with respect to their shape and nominal size and aspect ratio.

TABLE 1 Particulate additive characteristics

Shape	Type	Largest dimension (μm)	Aspect ratio
Sphere	Ballotini 5000	7	1
Fibre	Glass fibre OCF/497/ZZ	3000	70-100
Plate	Suzorite mica 200HK	<100	10-100
	Graphite X7181	<5	<10
	Fireclay ~70% Kaolin ~20% Mica (~10% Quartz)	<4	10-100 (1)

The Ballotini (spherical), glass fibre (unaxial) and Suzorite mica (biaxial) are relatively pure materials. The mica and glass fibre have a spread of aspect ratios enhanced by breakage during compounding. The fire clay is impure comprising 90% platey material and 10% spherical silica. The graphite has a low aspect ratio compared to mica and contains a fraction of material that can be regarded as being isotropic.

Incorporation of the additives into the polymer was carried out by two roll milling at 300°C. The rolled sheet was taken from the mill and cooled in a press. Measurements were either made on the rolled sheet or on injection mouldings produced from granulated compounded material.

An Arburg Allrounder IM machine was used to produce ASTM tensile bars (7" x ½" x 1/8") and side gated 1/8" thick, 4½" diameter discs. ASTM bars were used for tensile strength and flexural modulus measurements. With the discs the flexural modulus was measured in two directions 0° and 90° to the diameter line from the gate. The total energy required to break a disc was measured using an instrumented falling weight impact test.

Melt viscosity measurements were carried out using a Weissenberg Rheogoniometer Model R16 with the cone and plate configuration and oscillatory shear mode.

Measurements of linear expansion coefficient were made on the rolled sheet in three orthogonal directions with respect to the milling or rolling direction using a Mettler TA3000 Thermomechanical Analyser (TMA) system in the expansion mode. The TMA was set up using the standard procedure with a flat ended 3 mm diameter probe, a heating rate of 10°C min^{-1} and a load of 0.1N. Dynamic mechanical relaxation spectra were obtained from the same samples using a Dupont 981 Dynamic Mechanical Analyser (DMA) controlled by a Dupont 990 Thermal Analyser.

MECHANICAL PROPERTY ANISOTROPY

Table 2 compares the effect of spherical, platey and fibrous additives, at approximately equivalent loadings in the region of 50% weight, on the mechanical property anisotropy of injection moulded bars and discs.

TABLE 2 Effect of particle shape on moulding properties

		Flexural Modulus (GPa)				Tensile Strength	Falling Weight Impact Energy
			4 ½ Disc				
Filler Type	Wt % Filler	Bar	0°	90°	Anisotropy Ratio	MPa	(J) 4 ½ Disc
Control	—	10.2	9.8	2.9	3.40	168	6.25
Mica 200 Hk (Plate)	46	14.3	14.5	10.9	1.33	90	6.27
Glass Fibre (Fibre)	50	18.9	14.8	7.1	2.10	140	6.90
Ballotini 5000 (Sphere)	52	—	8.9	6.6	1.35	—	1.10

The ratio of the flexural moduli in the disc 0° and 90° directions termed the anisotropy ratio is reduced by all the particle shapes. In the case of the anisotropic particles the 0° modulus is increased by 50% compared to the unfilled polymer. Not surprisingly perhaps the plate is most effective in providing biaxial reinforcement in the plane of the disc having the largest 90° modulus. Assessment of the relative contributions to the modulus by the polymer and the particulate additive has not been attempted. However the properties of the bars do provide an indicator of the effect of the particles on polymer orientation. Tensile strength is particularly sensitive. The presence of glass fibre has the least effect on the SRP's ability to orient in the injection direction followed by the mica. Higher SRP orientation in the fibre case accounts for the higher modulus of the bar. The spherical Ballotini had a disastrous effect on the bar tensile properties. The bars broke when ejected from the mould hence no data was obtained. The embrittlement of the SRP is reflected in the poor impact properties of the discs containing Ballotini implying inhibition of long range molecular orientation. Both anisotropic fillers had a neutral effect on impact strength.

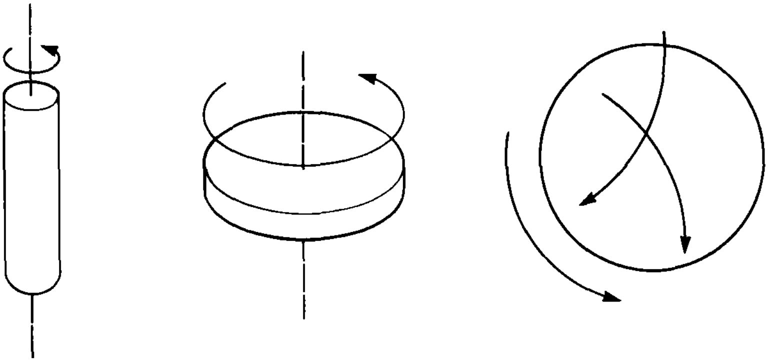


FIGURE 1 Fibre, plate, sphere rotation

Rotations, not involving displacement of polymer, available to each particle are shown in Figure 1. The long axis of the anisotropic particles will tend to align in the flow field. Axial rotation of the plates is probable and will depend on the nature of the flow. Random tumbling of spherical particles is highly likely. Assuming surface interaction between the particles and the melt then the observed relationships between mechanical anisotropy and particle shape can be accounted for.

MELT RHEOLOGY MODIFICATION

The rheology of main chain LCPs is complex. Only recently has progress been made in developing models that bring together the molecular parameters contained in the Leslie-Ericksen theory describing low mass liquid crystal flow and those intrinsic to the viscoelasticity of conventional polymer melts[7],[8]. These models go a long way towards explaining measurements of melt rheology[9],[5] and observations of sheared melt textural changes[10],[11].

An unsheared melt is assumed to have a polydomain texture as shown in Figure 2. In the so-called region I shear thinning at low shear rates corresponds to a reduction in domain size. The domains tumble in the flow, the rheology is paste-like and no net long range orientation is induced. Further reduction in domain size produces an increased surface area and a higher viscosity state is obtained. At higher shear rates a second shear thinning regime is entered domain size reduction reaches a lower limit and if the applied stress is sufficient domain coalescence and long range orientation can be achieved.

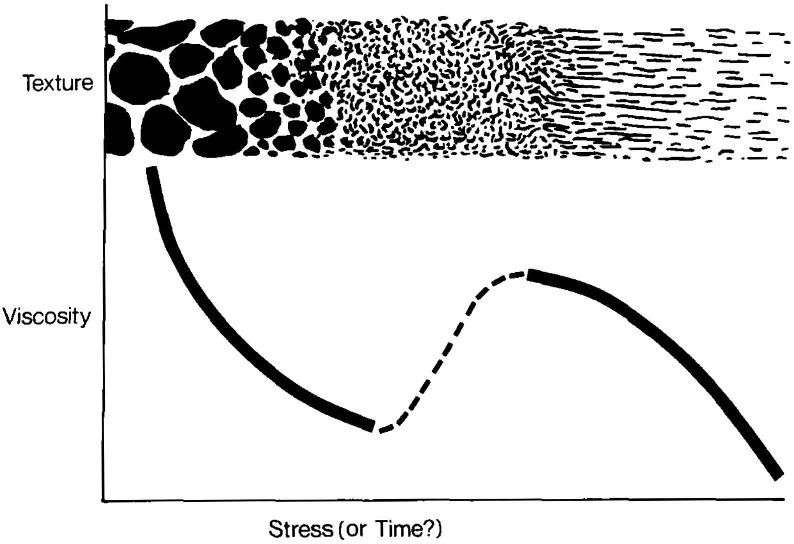


Figure 2 Viscosity and texture versus shear stress or rate

Figure 3 shows plots of complex viscosity versus frequency at 297°C for a range of concentrations of glass Ballotini spheres and platey mica. A small increase in viscosity with mica loading is observed, over the range 20-51% by weight. The presence of Ballotini spheres produces a large change in viscosity which is almost independent of concentration. For the unfilled

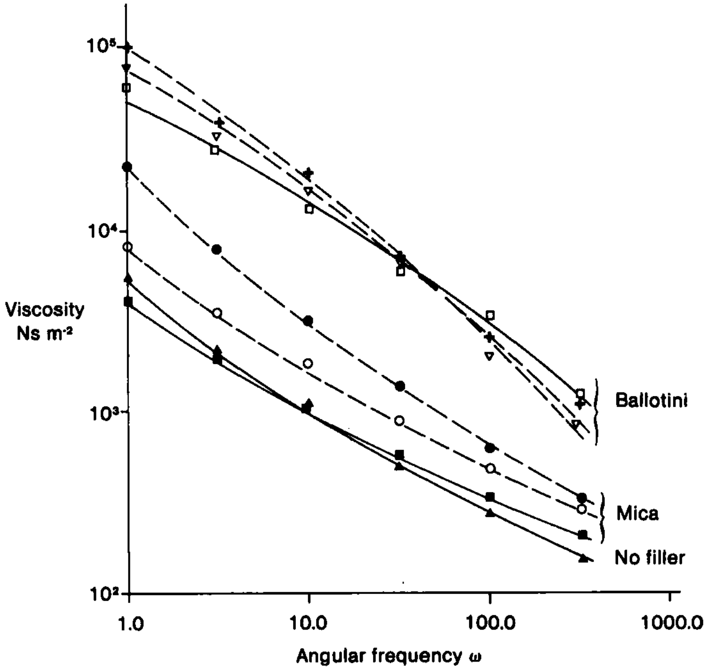


FIGURE 3 Complex viscosity versus frequency at 297°C for Ballotini concentrations; □ 27% ▽ 40% + 54% and mica concentrations; ■ 20% ○ 40% ● 51%

polymer and the mica containing samples the viscosity curves are concave upwards but those for the Ballotini containing samples are concave downwards. Comparison with the three region flow curve shown in Figure 2 suggests the onset of shear thinning is shifted to higher frequencies and paste-like flow is promoted by the presence of spheres. In other words the transition from domain tumbling to domain coalescence and long range orientation is inhibited. This is presumably a result of random tumbling of the spheres in the shear flow field. The observed effect of particle shape on mechanical properties is consistent with this picture.

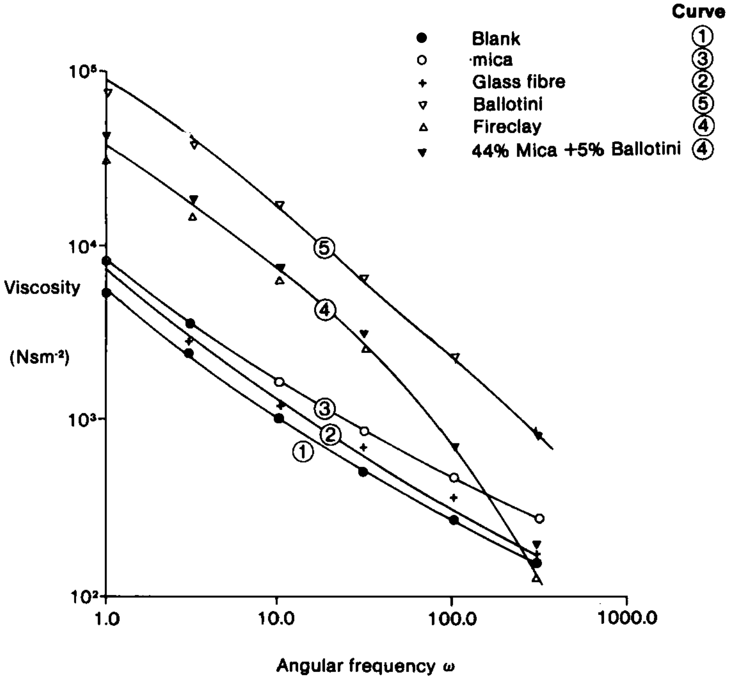


FIGURE 4 Complex viscosity versus frequency for 50% by wt. of various particulate additives at 297°C.

Figure 4 compares the effect of approximately 50% by weight of a wider variety of particulate additives. Glass fibre behaves similarly to mica producing a marginal increase in viscosity. Fireclay produced a large viscosity change. Although 90% of the composition of Fireclay is plate-like, 10% is spherical silica. It was suspected that this spherical component was responsible for the viscosity increase. The effect was reproduced by incorporating a mixture of mica and Ballotini into the polymer confirming the role of the spherical material.

EXPANSION COEFFICIENT ANISOTROPY

Samples of rolled and pressed polymer containing 0, 25 and 42% by weight of graphite were cut from the sheet. The faces were smoothed, polished and parallel. The directions of expansion coefficient measurement and nomenclature are shown in Figure 5.

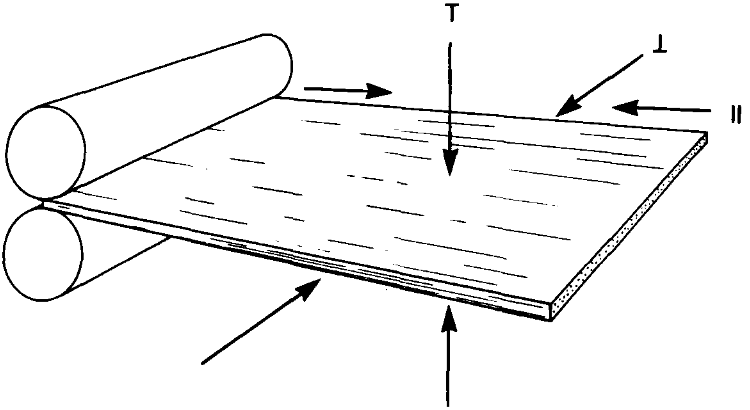


FIGURE 5 Expansion coefficient measurement directions

Initial measurements obtained by heating the samples from 40°C to 250°C at 10°C min^{-1} indicated that the observed expansion was a function of the previous thermal history of the sample which had been variable. The samples were annealed overnight at 150°C to ensure they had received the same thermal treatment. This appeared to improve the dimensional stability at temperatures below the annealing temperature although the properties changed above 150°C. Cooling the sample in the Mettler TMA from 250°C and re-running under the same conditions produced consistent results.

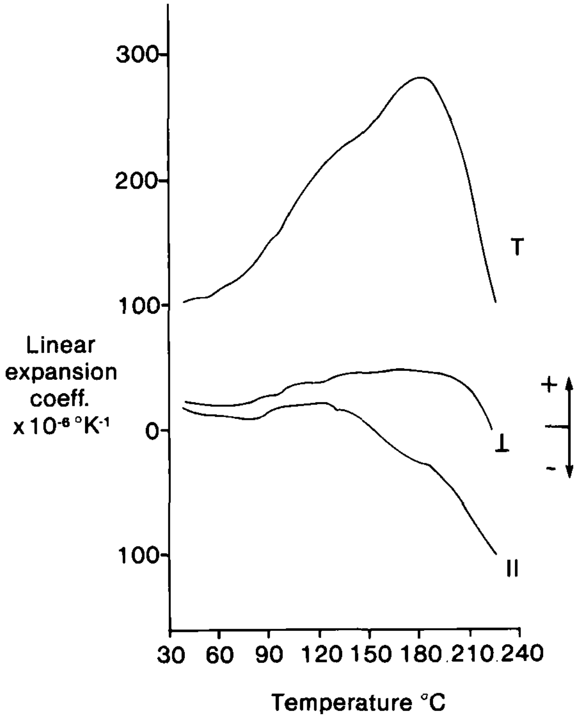


FIGURE 6 Expansion coefficient versus temperature for unfilled SRP

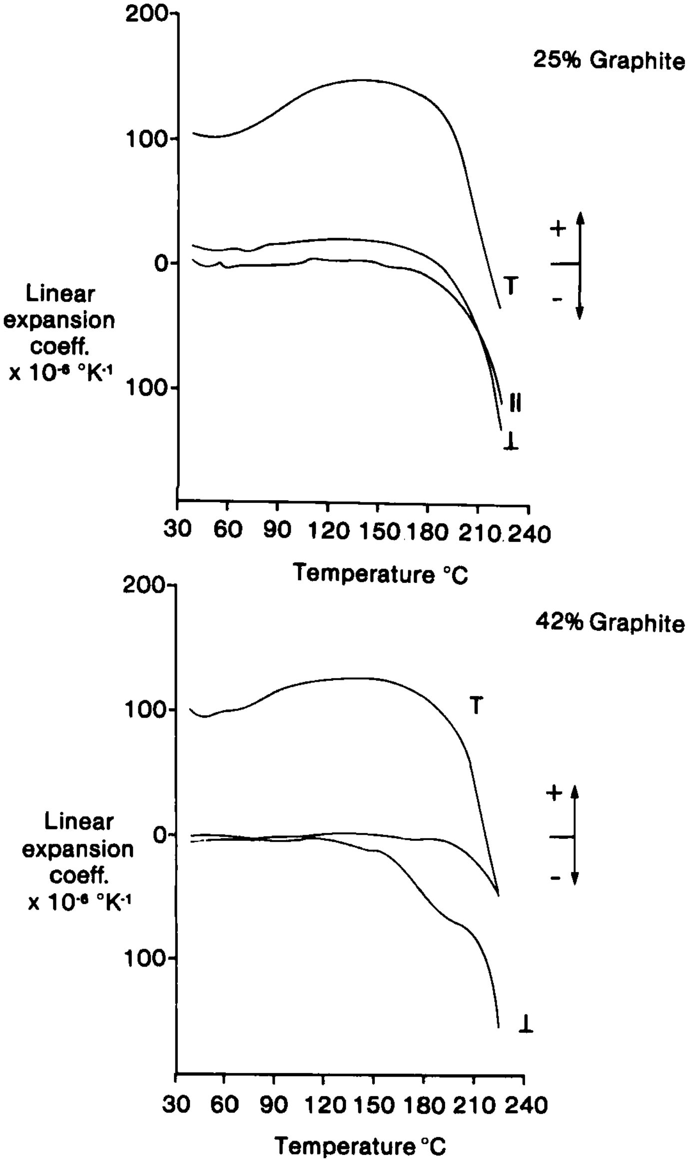


FIGURE 7 Expansion coefficient versus temperature for SRP containing 25% and 42% graphite.

The results shown in Figures 6 and 7 are from re-run samples. Expansion perpendicular to the plane (T) is greater than in the other directions for all graphite concentrations and is of the same order as conventional polymers. The unfilled polymer shows an increase to 280×10^{-6} at 180°C with a decrease thereafter. The initial expansion coefficient at 40°C is almost independent of graphite content but the maximum value is only approximately half that of the unfilled polymer and occurs at ∿ 140°C. With increasing temperature the expansion rate decreases and shrinkage occurs in both the 25% and 42% sample above 220°C.

Results obtained both perpendicular and parallel to the rolling direction generally show a reduction in expansion with increasing graphite content in the range 40°C to 120°C. Higher loadings give enhanced dimensional stability and balancing of the expansion behaviour in the plane. At temperatures above 150°C expansion perpendicular to the plane is accommodated by shrinkage in the machine direction in the unfilled polymer case. The presence of graphite inhibits shrinkage in the machine direction and is replaced by shrinkage in the transverse direction which becomes increasingly dominant with increasing graphite content.

DYNAMIC MECHANICAL LOSS SPECTRA

Dynamic mechanical damping tan δ spectra of the compounded, rolled and pressed sheet have been obtained from rectangular samples 25 mm x 10 mm cut with the long axis both perpendicular and parallel to the rolling direction. The results shown in Figure 8 were obtained in the range 0°C to 220°C at a heating rate of 5°C min^{-1}. The β transition in the region of 60°C and the α transition at about 110°C of the 6-oxy-2-naphthoyl unit containing SRP being studied has been identified by Yoon and Jaffe[12]. The β process is associated with reorientational motion of the 2,6 naphthalene moiety. Dielectric loss measurements indicate the neighbouring carbonyl groups are also involved[13]. The α process behaves similarly to the glass transition in conventional polymers, except the strength is significantly lower, and has been associated with cooperative motions along the chains.

The effect on tan δ of approximately equal volumes, 20-25%, of Ballotini glass spheres, glass fibre and mica plates, measured parallel and perpendicular to the rolling direction, is shown in Figure 8. The spectra have three distinct regions, the β transition at 60-80°C, the α transition at around 120°C and a region of increasing damping from 160-220°C. In general tan δ is lower measured 0° to the milling direction, across the full temperature range, with less of a difference at the higher temperatures. The 0° spectra shows that both glass fibre and mica produce an equal reduction in the β transition intensity compared to both the unfilled polymer and the α transition; Ballotini slightly increases the β transition strength.

The α transition shows a small reduction in strength and a small shift to a higher temperature for the mica and glass fibre and a small increase in strength and a shift to a lower temperature for the Ballotini. In the range 160-220°C the glass fibre shows a bigger increase in tan δ than the mica with both showing greater damping than the unfilled polymer. Damping in this region is suppressed relative to the polymer by Ballotini.

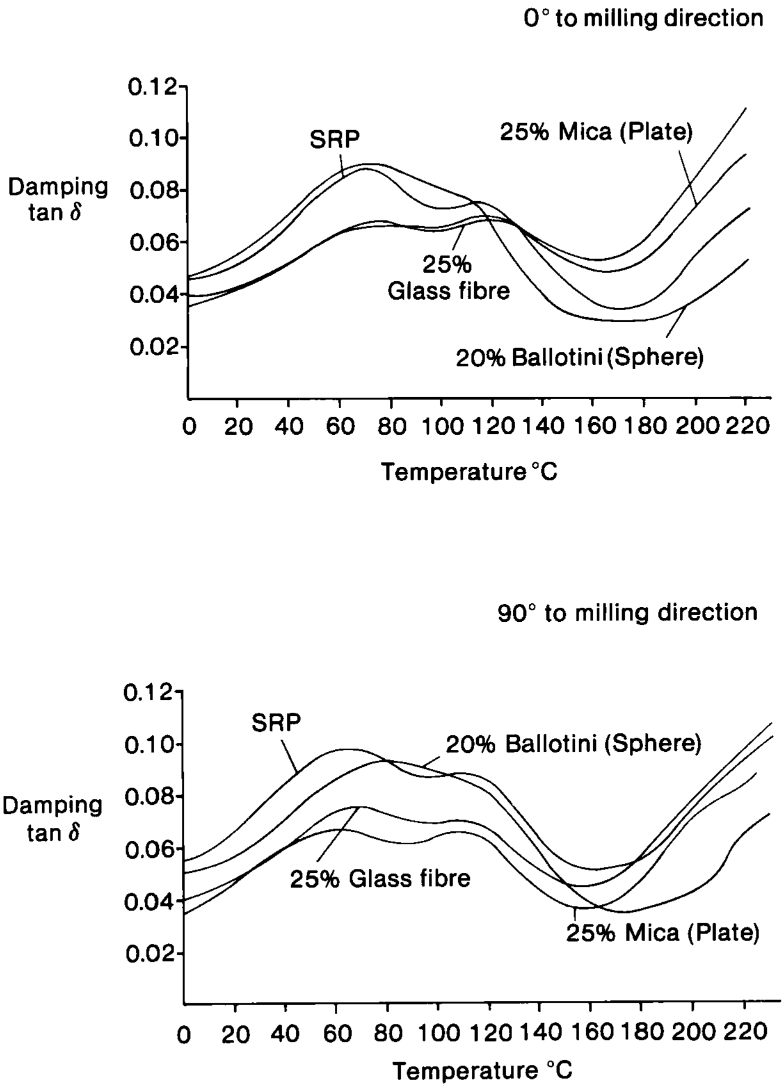


FIGURE 8 Damping tan δ versus temperature

90° to the milling direction the α peak intensity is depressed by the mica and glass fibre relative to the unfilled polymer, to a value equivalent to that measured in the 0° direction. The peak position is independent of the filler shape and is ∿10°C lower than in the 0° case. The 0° and 90° α peak temperatures for the Ballotini are approximately equal. This implies molecular orientation in the Ballotini sample is less anisotropic than in the glass fibre, mica and unfilled polymer samples.

The β peak temperature in the 90° direction for the unfilled polymer and glass fibre are the same as in the 0° direction. The mica α peak is shifted to a slightly lower temperature and that of Ballotini to a higher temperature. The β peak intensity is equivalent in the 0° and 90° directions for the mica sample. Glass fibre is less effective than the mica in depressing the β transition strength in the 90° direction. In the range 160-220°C the trends in the 90° direction are similar to those observed in the 0° direction.

Figure 9 shows the effect of graphite content, measured in the 0° direction. There is a marked decrease of the β peak intensity, particularly for the 25% sample, a smaller suppression of the α peak intensity and an increase in damping in the 160-240°C range with increasing graphite content.

It is interesting to correlate the temperature dependence of the tan δ spectra with that of the expansion coefficient data. Account must be taken of the difference in frequency of the tests. The DMA frequency in the region of the α and β processes is of the order of 20 Hz. That of the TMA will be approximately two order of magnitude slower

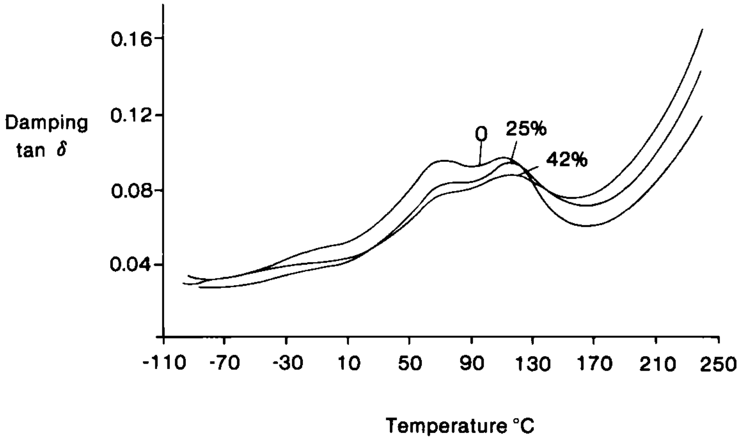


FIGURE 9 Damping tan δ versus temperature for SRP containing 0,25 and 42% graphite

which would produce a downward temperature shift of 10-20°C.

Comparing Figures 6 to 9 and the effect of graphite content, it can be seen that the suppression of the increase in expansion coefficient perpendicular to the plane correlates with a decrease in the β transition strength. This can be interpreted as inhibition of the effect of reorientational motions of the naphthalene moiety on the polymer conformation. Balancing of the expansion coefficient parallel and perpendicular to the milling direction in the plane of the sheet corresponds to a balancing of the β peak intensity. A change in the expansion coefficient in the region of 90-100°C for all measured directions corresponds to the α transition. The increase in damping from 150°C to 220°c correlates with the accelerated decrease in expansion coefficient. Both the unfilled polymer, measured parallel to the milling direction, and the 42% loaded sample, measured in the perpendicular direction, show a discontinuity at

∿180°C. This suggests that a process producing a positive expansion is occurring superimposed on the underlying contraction. It is proposed that the expansion is due to partial melting of crystallinity in the polymer. This also enables an increase in intermolecular sliding motions the onset of which occurred at the α transition.

Figure 10 attempts to illustrate the various effects. The graphite surfaces constrain intramolecular conformational changes and intermolecular sliding. The latter effect in particular would account for the reversal in the dominant contraction direction from paralled to the flow to the transverse direction with increasing graphite content. Long range polymer orientation is not uniaxial in any of the samples studied and the presence of the graphite probably promotes orientation in directions other than the milling direction by axial rotation. If the graphite surface

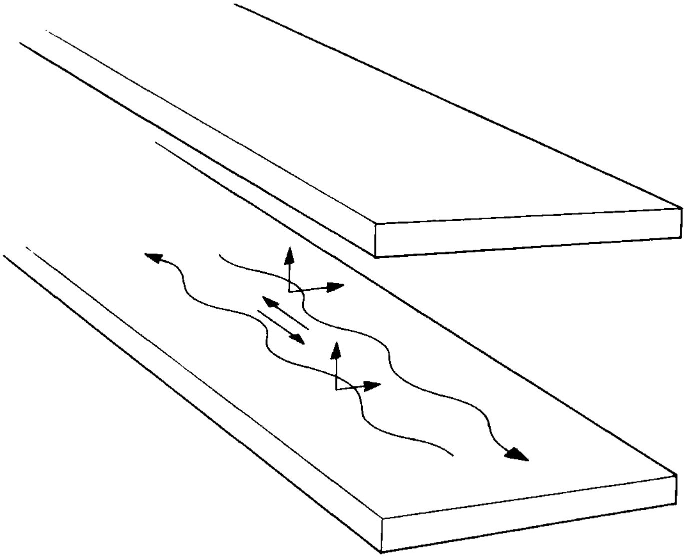


FIGURE 10 SRP motions constrained by plates.

preferentially retards sliding in the milling direction then sliding in the transverse direction would become increasingly important as is observed.

CONCLUDING REMARKS

The processability and properties of main chain LCP's can be substantially modified by the incorporation of particulate additives and is highly dependent on particle shape.

Fibres - The presence of fibres in an SRP melt enables modification of property anisotropy under injection moulding conditions but does not have a large effect on the ability of SRPs to orient or on the melt viscosity. Fibres produce some biaxial balancing of properties. For example disc modulus anisotropy is reduced. The β process is suppressed parallel and perpendicular to the flow with a greater reduction in the former direction.

Plates - Plates also enable property modification without a large effect on SRP orientability or melt viscosity (except when isotropic contaminants are present). SRP orientation transverse to the flow direction can be more readily achieved with plates than with fibres under conditions which promote axial plate rotation. Biaxial balancing of properties is more readily achieved. For example the β transition, expansion coefficient and modulus can be equalised in the plane of a moulding.

Spheres - Spheres reduce property anisotropy by inhibiting long range orientation. Tumbling of spheres in a flow field hinders melt viscosity reduction by shear thinning and domain coalescence. Smooth, high surface area spheres such as Ballotini represent the worst case.

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