

Influence of Fillers on the Mechanical Response of an Amorphous Liquid-Crystalline Polymer

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ABSTRACT: A semirigid and amorphous commercial liquid-crystalline copolyester (Rodrun) was filled with mica and calcium carbonate (up to 25 wt %) by direct injection molding. The fillers led to decreases in the processability, as observed by torque increases, but maintained the thermal resistance of Rodrun. The effects of the two fillers on the modulus of elasticity, ductility, and tensile strength were the same or very similar. The decrease in the tensile strength (20% for a 10% filler content) was compensated by a gener-

ally slight increase in the modulus of elasticity, whatever the filler content was. This balance of properties found in these new liquid-crystalline-polymer-based materials and the important savings that the fillers bring may spread the applications of these materials' matrices. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 998–1003, 2003

Key words: liquid-crystalline polymers (LCP); fillers; thermal properties; mechanical properties

INTRODUCTION

Thermotropic liquid-crystalline polymers (LCPs) are linear-chain thermoplastics mainly characterized by a high degree of molecular alignment in the melt state, which is due to the high rigidity of their chains. This orientation of the melt chains can be frozen in the solid state, and this gives rise to exceptional mechanical properties in the direction of orientation. Moreover, their usual low melt viscosities make these materials very attractive for injection molding. Other advantages of LCPs include their excellent chemical and thermal resistance as well as good barrier properties. All these properties explain the attention that these materials and their blends have attracted in the last several years^{1,2} and probably will attract in the future.³

Among the disadvantages, the processing temperatures are usually high because of the rigidity of the molecules. For this reason, semirigid and low-performing LCPs, with lower processing temperatures and glass-transition or melting temperatures,^{2,4,5} have been developed. Moreover, the mechanical properties are poor in directions other than that of the orientation, giving rise to highly anisotropic final products. Finally, they have been very expensive materials.

The addition of fillers has been used^{6–14} to overcome these disadvantages. The low viscosity of LCPs, particularly the semirigid ones,¹⁵ makes them attractive candidates as matrices for filled polymers. The addition of inorganic fillers strongly diminishes the raw material cost and, in some cases, could improve some thermomechanical properties. This is despite the fact that the effects of the fillers on the mechanical properties of the LCP–filler composites are smaller than those for conventional thermoplastics.⁹ Moreover, the anisotropy may be reduced. These potential advantages have given rise to the development of commercial filled LCPs.

In filled LCPs, the influence of the processing parameters and filler content on the thermomechanical properties^{7,9–11} is most often studied. Typically, as the filler content increases, moderate decreases in the tensile strength and increases in the stiffness are obtained, along with improved thermomechanical properties and a lower level of mechanical and thermal anisotropy.^{9,13,14}

The aforementioned studies are all of semicrystalline LCPs, mainly Vectra. However, the effects of filler addition on the thermomechanical properties of semirigid and amorphous LCPs have hardly been studied, with the exception¹¹ of a semirigid LCP copolymer (SBH 112, Eniricerche) in which the influence of the filler type (wollastonite, magnesium dioxide, and glass fibers) on the thermal and mechanical properties was studied. Remarkable increases were obtained, but the properties of the pure LCP, used as a reference, were very poor, probably because of the compression molding used as the processing method, which prevented fibrillation.

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TABLE I
Chemical Composition and Size Distribution
of Mica and Calcium Carbonate Particles

	Composition		Size distribution
Mica	SiO ₂	48%	>32 μm: 0.5%
	Al ₂ O ₃	34%	>20 μm: 8%
	K ₂ O	9.5%	>10 μm: 11%
	Others	8.5%	>5 μm: 45%
			<5 μm: 55%
Calcium carbonate	CaCO ₃	99.0%	>44 μm: 0.05%
	MgCO ₃	0.5%	>2 μm: 58%
	Others	0.5%	<2 μm: 42%

Rodrun LC-3000 (Ro; Unitika, Ltd., Tokyo, Japan) is an amorphous and semirigid LCP that shows a low processing temperature (200–220°C) because of its low glass-transition temperature (60°C). However, the effects of the addition of fillers on its thermal and mechanical properties have not been studied. In this work, Ro was filled with up to 25 wt % mica or calcium carbonate. The morphology of the composites was studied with scanning electron microscopy (SEM), the behavior at high temperatures was studied via the heat deflection temperature (HDT), and the mechanical properties were studied by means of tensile testing in both the longitudinal and transverse directions.

EXPERIMENTAL

The LCP used as a matrix was Ro, a semirigid poly(ethylene terephthalate-*p*-hydroxy benzoic acid) (40/60) copolyester. Two different fillers were employed: mica (dry and ground DG-10/20, Delta Tecnic SA, Barcelona, Spain) and calcium carbonate (Omycarb 2-BE, Clarianacal SA, Zaragoza, Spain). The chemical compositions and size distributions of the particles are shown in Table I.

The Ro pellets and filler particles were dried for 16 h at 80°C, mixed in the desired weight ratios (5, 10, 20, and 25%), and tumbled together before the injection molding. The mixtures were directly injection-molded in a Battenfeld BA 230E (Kottingbrunn, Austria) reciprocating-screw injection-molding machine. The screw of the plasticization unit had a diameter of 18 mm, a length/diameter ratio (L/D) of 17.8, a compression ratio of 4, and a helix angle of 17.8°. The melt and mold temperatures were maintained at 220 and 20°C, respectively, and the injection rate was 10 cm/s. ASTM 648 HDT specimens and quadrangular plaques (64 mm × 64 mm × 1.5 mm) were obtained. ASTM 638 type V tensile specimens were machined both parallel and perpendicular to the direction of the flow advance at the center of the plaque.

The torque of blending was measured for the Ro-filler systems in a Brabender PLE650 plasticorder (Du-

isburg, Germany) at 220°C and at a rotation speed of 30 rpm. The torque values corresponded to a mixing time of 12 min when a steady torque was obtained.

The HDT values of the composites were measured with an ATS-FAAR MP3 HDT tester (Milan, Italy) at a heating rate of 2°C/min according to ASTM 648.

Tensile testing was carried out on an Instron 4301 tester (Canton, MA) at a crosshead speed of 10 mm/min under room conditions (23 ± 2°C and 50 ± 5% relative humidity). The mechanical properties—Young's modulus and the break stress and strain—were determined from the force-displacement curves. At least eight specimens were tested for each determination. The tensile fractured surfaces were observed by SEM (Hitachi S-2700, Tokyo, Japan) at an accelerating voltage of 15 kV after gold coating.

RESULTS AND DISCUSSION

Processing and thermal properties

The filler must reduce the processability of LCPs because the solid particles hinder the flow. Moreover, sometimes the temperature resistance is increased because of fillers. For these reasons, the processability and temperature resistance of the unfilled and filled Ro samples were compared by the measurements of the torque needed in a Brabender mixer and by means of HDT tests.

In Figure 1, the torque of mixing after a mixing time of 12 min is shown against the filler volume content. The torque clearly increased with the filler content, reaching a value double that of the neat Ro at an approximate filler volume content of 14%. Similar or even higher torque increases have been observed in other filled LCPs^{11,16} and also in fiber-reinforced LCPs.¹⁷ Moreover, the torque increases were very similar for the two fillers at the same filler content. This indicates that, in this case, neither the

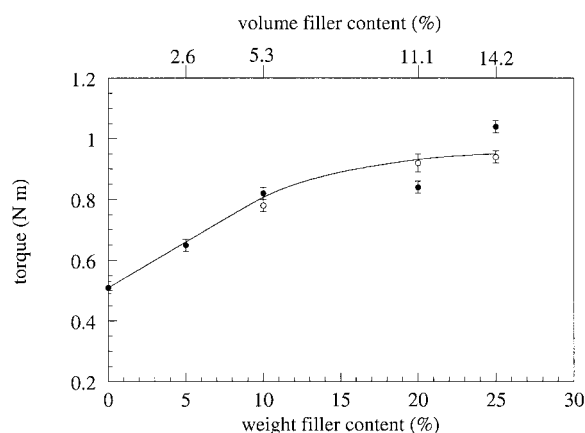


Figure 1 Torque of (○) mica-filled and (●) CaCO₃-filled Ro after a mixing time of 12 min versus the filler volume content.

morphology of the filler nor the particle size had much influence on the viscosity of the composite. However, in a previous work,¹¹ a higher L/D ratio of the filler gave rise to a greater torque increase. This is the opposite of what can be seen in Figure 1 because the planar mica particles had a higher L/D value than those of calcium carbonate. Therefore, if a larger L/D ratio leads to a higher torque, it should be counteracted, for instance, by a possible lower adhesion level with the Ro.

The HDT of the CaCO_3 -filled Ro showed a negligible increase (1–2°C) with the filler content. No significant changes took place for mica-filled Ro either. An increase in HDT or other properties, used to measure the temperature resistance, is usually seen in semicrystalline polymers with the addition of fillers. However, amorphous and semirigid LCPs, such as filled amorphous thermoplastics,¹⁸ are much less affected, showing slight increases^{11,17} comparable to those of the nonfibrous fillers of this work.

Morphology

The orientation of the LCPs, both in the skin and in the core, and the dispersion and surface of the fillers were observed by SEM on the fracture surfaces of the tensile specimens. The morphology in the direction of the flow of the skin of the 10% CaCO_3 composite is shown in Figure 2(a), and that of the core is shown in Figure 2(b). The morphology of the LCP did not change with either the filler nature or content. The highly oriented morphology of the skin, which was qualitatively similar to that of the neat Ro, contrasts with the much less defined orientation of the core. As can be seen in Figure 2(b), the core of the specimen was not orientation-free because several short fibril ends came away from the fracture surface.

As also shown in Figure 2(a,b), there were no particles to be seen at all in the skin, probably because they were occluded by long fibrils. The presence of particles in the skin is seen and measured later. Details of mica and CaCO_3 particles are shown in Figure 3(a,b), respectively. The surface of the mica particles [Fig. 3(a)] was completely defined, and no signs of either debonding or a matrix residue were present. This indicates that there was practically no adhesion between the mica and the matrix. For CaCO_3 , the fracture surface was less defined. The adhesion was not, however, relevant because adhered LCP protruding from the particle surface was not seen. A slight adhesion of the CaCO_3 particles may influence the similar torque values of both composites of this work; this was observed despite the larger L/D ratio of the mica particles.

The fracture surfaces in the direction perpendicular to the flow of both the skin and core of the CaCO_3 -filled composites are shown in Figure 4(a,b), respec-

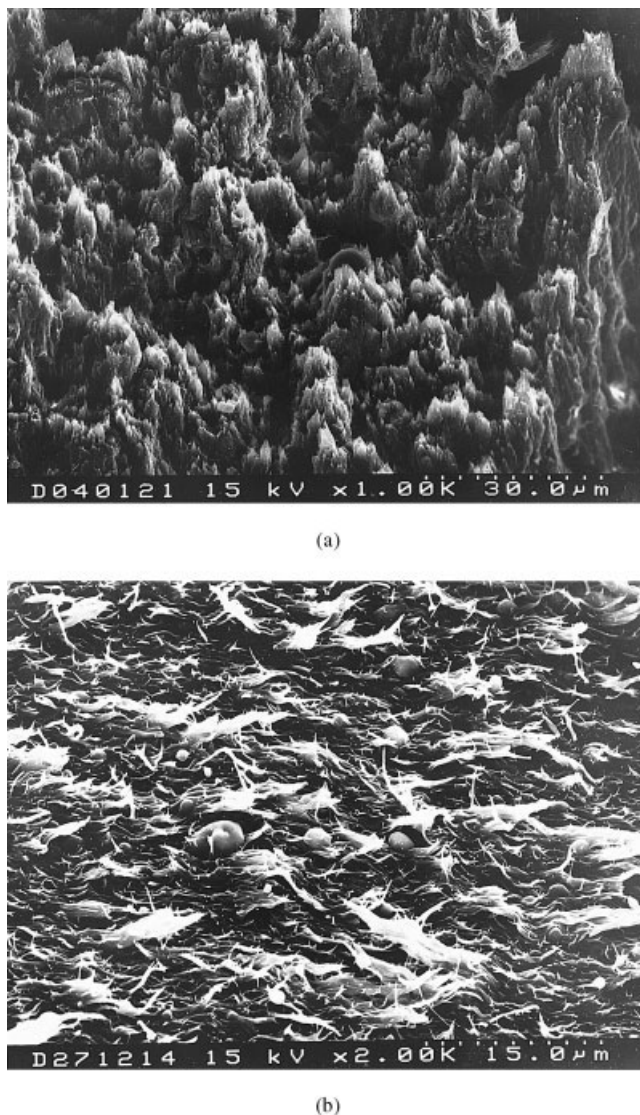
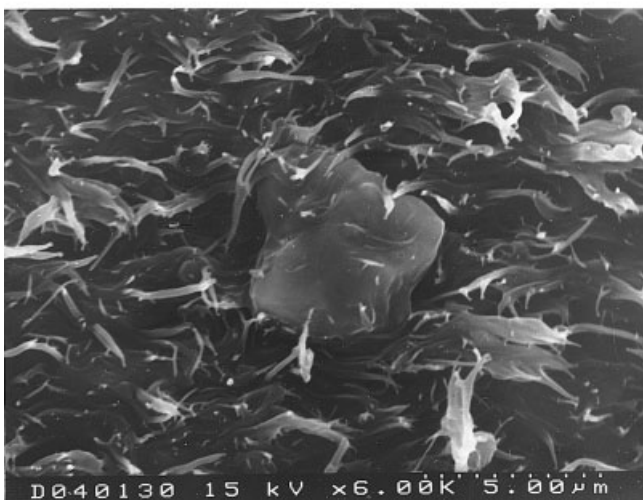


Figure 2 Morphology in the direction parallel to the flow of representative zones of (a) the skin and (b) the core of 10% CaCO_3 -filled Ro.

tively. As can be seen particularly in Figure 4(a), there was a clear rootlike morphology that lay horizontal in the fracture surface, that is, parallel to the flow direction, indicating significant fibrillation. The particles were present both in the core and in the skin, and their presence did not seem to hinder fibrillation. However, the distribution of the filler particles was not clear because of the high density of fibers. It could be heterogeneous because the very different flow conditions of the skin and core could lead to different filler contents in these two zones. For this reason, small parts of the skin and core of the specimens were calcinated, and the filler content was measured. The variations observed were negligible, so the filler contents of the skin and core were the same and corresponded to the bulk filler content.



(a)



(b)

Figure 3 Details of (a) mica and (b) CaCO₃ particles of 10% filled composites.

Mechanical properties

Young’s moduli of the composites in parallel and perpendicular directions versus the filler content are shown in Figure 5 for the CaCO₃ and mica fillers. The anisotropy in the modulus, measured as the relation between the modulus in the parallel direction and the modulus in the perpendicular direction (E_{par}/E_{perp}), is also shown. The moduli in the parallel direction of mica- and CaCO₃-filled Ro were fitted by two curves that could also be considered a single curve if the standard deviation of the values was considered. For the perpendicular direction, a single curve was fitted to the values of both the mica-filled and CaCO₃-filled Ro. The dispersion of the modulus data was quite high, indicating a slight variable dispersion of the filler among the specimens. A good dispersion was helped by the low maximum filler volume content

(14%). As can be seen, and despite the presence of the inexpensive fillers, the modulus of elasticity of the composites, in both the parallel and transverse directions, was rather similar to or slightly higher than that of neat Ro. As a result, as can be seen in Figure 5, the anisotropy of the LCP was maintained in the composites. This agrees with the small influence of the fillers on the orientation of an LCP seen in another LCP–filler study.^{8,10} Finally, the fact that the modulus of elasticity of the composites was similar to or slightly higher than that of the neat LCP was highly significant because of the negligible price of the filler compared with that of the LCP. This means that the price of the composite was reduced by a proportion similar to the filler volume content.

The similar modulus values of composites of the two fillers indicated that neither the particle shape nor



(a)



(b)

Figure 4 Morphology in the direction perpendicular to the flow of representative zones of (a) the skin and (b) the core of 10% CaCO₃-filled Ro.

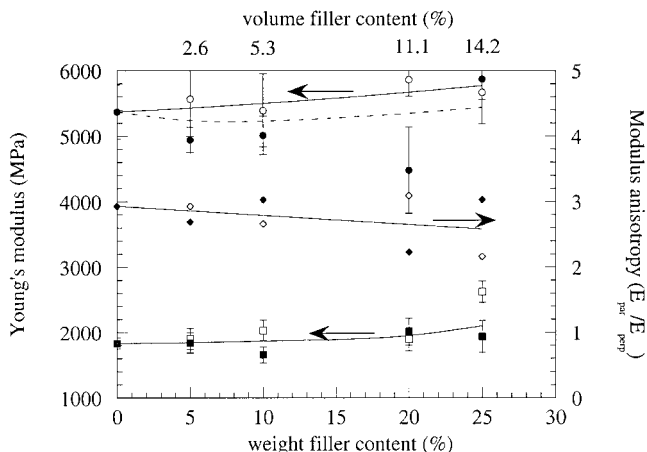


Figure 5 Young's modulus values in the directions (\circ, \bullet) parallel and (\square, \blacksquare) perpendicular to the flow and (\diamond, \blacklozenge) anisotropy of Ro-filled composites versus the filler content. Empty symbols represent mica, and filled symbols represent CaCO_3 .

the nature of the filler had a relevant influence on Young's modulus. However, as can be seen in Figure 5, the modulus of elasticity in the parallel direction slightly increased in the case of mica with increasing filler contents. This was probably not due to a different orientation of the LCP in the filled and unfilled materials because it is usually similar in other LCP-filler composites.^{8,10} Therefore, the observed behavior was probably due to the large L/D ratio of the mica particles in comparison with that of CaCO_3 and to their mostly parallel orientation in the skin, which was discussed in the Morphology section. Moreover, the filler-matrix adhesion was low but probably sufficient to allow stress transmission at the very low strains at which the modulus of elasticity was measured. When another semirigid LCP¹¹ was filled with both wollastonite and magnesium carbonate, although the values of the modulus (0.5 GPa) and tensile strength (11.5 MPa) were not those associated with either an LCP or a thermoplastic, the increase in the modulus was significant only at filler contents higher than those of this work. Glass fibers with a high L/D ratio increased the modulus even at low concentrations.

The elongation at break in the parallel and perpendicular directions of Ro filled with both calcium carbonate and mica is shown in Figure 6. Data for the ductility of LCPs in the transverse direction are not available in the literature to our knowledge. As can be seen, the ductility in the transverse direction was rather high, leading to the presence of yield and necking in the specimens. It was higher than in the parallel direction, both in the pure Ro and in the composites. This may be due to the very low possibility of elongation in the parallel direction of the already almost fully elongated molecules. The ductility decreased slightly with the filler in the parallel direction. For the

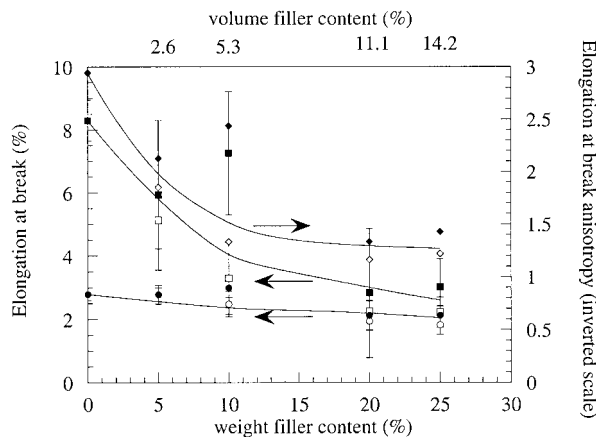


Figure 6 Ductility values in the directions parallel and perpendicular to the flow and anisotropy of Ro-filled composites versus the filler content. See Figure 5 for an explanation of the symbols.

transverse direction, the ductility clearly decreased as a result of the presence of the undeformable filler particles oriented just in the direction transverse to the applied external load, thereby noticeably affecting the fracture properties. These ductility values were independent of the shape of the filler despite the larger and thinner shape of the mica particles, which should lead to more important stress concentrations at the tip of the particles and to premature failure. The decrease in ductility by itself is not important in LCP materials because of their inherent fragility, unless it influences the tensile strength values, which have more practical relevance.

The tensile strength values of the composites filled with CaCO_3 and mica are shown in Figure 7. The tensile strengths of both composites in the parallel direction could be fitted to a single curve. Although a single curve could also be plotted, two curves were

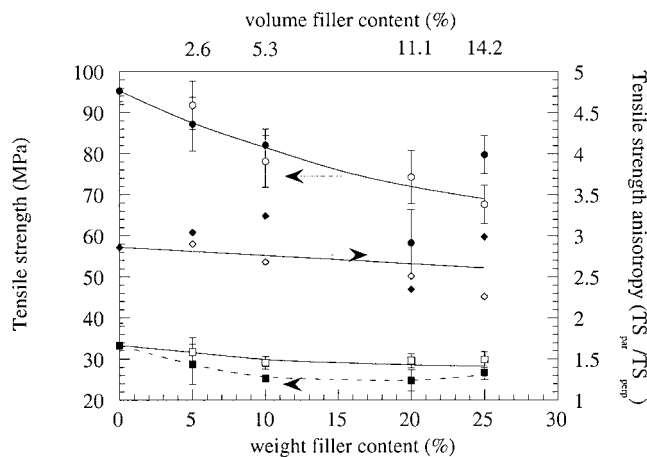


Figure 7 Tensile strength values in the directions parallel and perpendicular to the flow and anisotropy of Ro-filled composites versus the filler content. See Figure 5 for an explanation of the symbols.

plotted for the perpendicular direction. As can be seen and as was expected, the tensile strength decreased with increasing filler contents in both directions. For the parallel direction, it must be a result of the ductility decrease with both mica and CaCO_3 , which made the stress-strain curves shorter, thereby leading to a smaller maximum stress. Slight tensile strength decreases were also observed for Vectra-wollastonite composites.⁸ For the transverse direction, the ductility decrease had less influence on the height of the tensile curve than could be expected from the ductility decrease because the specimens broke close to the yield point. However, the effect of the ductility decrease was high enough to counteract the slight increase in the modulus of Figure 5.

CONCLUSIONS

Homogeneously filled Ro composites were obtained by direct mixing in an injection machine. The increase in the viscosity of the Ro with the addition of a filler did not depend on the nature of the filler but only on the filler content. Unexpectedly, the thermal resistance of the Ro was not affected by the addition of the fillers, as determined by the HDT measurements. The tensile properties of the LCPs were only slightly changed by or were independent of the nature and morphology of the fillers. The large ductility in the perpendicular direction was the property most sensitive to the fillers. The fillers gave more brittle materials with smaller tensile strengths (20% decrease for a 10% filler content) but with a modulus of elasticity that was the same as that of neat Ro or even slightly increased in the case of mica, despite the important economic advantage that

the use of fillers brings. This improved property-price balance extends the applications of these materials.

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