

Liquid Crystal Polymer-Based Blends: "Universal Grade" Polymers?

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SYNOPSIS

Polymeric materials can be easily processed with different processing operations thanks to suitable rheological properties. Melt flow index, or grade, which is a measure of the fluidity of the polymers, is the most commonly parameter used to characterize the polymers from the point of view of their melt viscosity. Injection molding requires high grade materials, whereas low grade values are best suited for extrusion. Of course, it would be no doubt of interest if single "universal grade" materials could be used for all processing operations. In this paper it is demonstrated that the blends of low grade polymers with small amounts of liquid crystal polymers can be conveniently used for all processing operations. Mechanical and thermal properties of the polymer matrix are in general retained or, in some cases, improved.

INTRODUCTION

The great majority of commercially available thermoplastic polymers are normally worked up into different marketable forms, thanks to the possibility of processing them with different processing operations. For example, poly(ethylene terephthalate) (PET) is used for production of melt-spun fibers, extrudates, blow- or injection-molded articles, etc. However, the characteristics of each thermoplastic material need to be optimized in view of the processing operation to be used, so as to obtain the best properties and performances of the finished objects.

The processability of thermoplastic polymers is related to their rheological behavior, and this depends, in turn, not only on the structural characteristics (chemical structure, branching, etc.) but also on the molecular weight (MW) and, to a lesser extent, on the molecular weight distribution (MWD). Thus, polymers having high elongational viscosity are required for processing techniques such as melt spinning or film blowing, in which elonga-

tional flow is involved. On the other hand, for the injection molding, low melt viscosity materials are needed, in order to grant an easy and complete mold filling, as well as fast processing cycles.

All commercial thermoplastics are usually made available on the market with several molecular weights, so as to fit at best the different processing treatments.

The parameter most commonly employed to characterize from the point of view of their melt viscosity is the melt flow index (MFI), or grade, which is a measure of the fluidity of the molten polymers. Therefore, the higher grade polymers are best suited to injection molding, whereas the lower grade ones to melt spinning or blowing operations.

Although all manufacturers of thermoplastic materials are already prepared to market different grades of the same polymer, it would be no doubt of interest if a single "universal grade" could be processed with all the known techniques, upon the simple *in situ* addition of small amount of a second component playing the role of adjusting the processing characteristics of the polymer, without imparting the mechanical properties of the finished objects.

During the last few years, a great number of patents and scientific papers have been published by

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industrial and academic research laboratories, describing the effect of blending relatively low amounts of liquid crystal polymers (LCPs) with commercial thermoplastic materials.¹⁻¹³ The effects most commonly observed are that LCPs lower the melt viscosity and enhance the tensile modulus and strength of the thermoplastic polymers, thus lending themselves for use as processing aids and reinforcing agents.

In our laboratories, a number of blends of both wholly aromatic and semirigid LCPs with different thermoplastic polymers have been studied.¹⁴⁻²⁰ The results of the previous investigations, together with new data, are discussed here with the aim of demonstrating that LCPs may be considered as candidate modifiers of commercial thermoplastics in view of the use of a single grade of these latter for any of the known processing operations.

EXPERIMENTAL

The polymers used in this work are reported in Table I. Bisphenol-A polycarbonate (PC), nylon 6 (Ny), and polypropylene (PP) were used as thermoplastic matrices for the blends. LCP1 is a semirigid copolyester made from sebacic acid, 4,4'-dihydroxybiphenyl, and 4-hydroxybenzoic acid in the molar ratio 1 : 1 : 2. Synthesis and properties of this copolyester have been already presented.²¹⁻²³ LCP2 is a wholly aromatic copolyesteramide made from 6-hydroxy-2-naphthoic acid (60%), aminophenol (20%), and terephthalic acid (20%). The chemistry and the properties of this type of copolyesteramide have been already presented.²⁴⁻²⁶

All the blends were prepared by extrusion in a laboratory extruder ($D = 19$ mm, $L/D = 25$) Brabender equipped with a die assembly for ribbon. The LCP content c varied between 1 and 20%. The pure

polymers were also subjected to the same treatment. The die temperature was 290°C for PC and Ny blends and 240°C for PP blends. Before extrusion, all the materials were carefully dried at 120°C under vacuum for at least 24 h.

Melt spinning was carried out using the tensile module of a capillary viscometer, Rheoscope 1000 (Ceast, Italy), equipped with a capillary of 1 mm and length to diameter ratio of 40. The extrusion temperature was 260°C for all the investigated materials. The draw ratio, DR, was evaluated as the ratio between the cross sections of the die and of the filament.

Injection molding experiments were carried out using a Negri and Bossi reciprocating screw injection molding machine, Model N25, with a clamping force of 25 tons and a maximum size of 50 cc. The operating conditions for PC1/LCP blends were: injection temperature 305°C, mold temperature 80°C, and constant injection flow rate 10 cc/s. The operating conditions for PP1/LCP1 blends were: injection temperature 240°C, mold temperature 80°C, and constant injection flow rate 8 cc/s.

Rheological measurements were carried out with a capillary viscometer Rheoscope 1000 equipped with a capillary of 1 mm in diameter and length to diameter ratio of 40. Stress-strain curves were determined on filaments and strips cut out from the ribbon using an Instron Model 1122. Impact strength measurements were made on notched samples using a Fractoscope apparatus (CEAST) in the Izod mode. Dynamic-mechanical measurements were obtained using a Rheovibron viscoelastometer Model DDV IIB. The heating rate was about 1°C/min and the frequency 110 Hz.

RESULTS AND DISCUSSION

The flow curves of all the investigated materials are shown in Figures 1-3. For all the systems, it was found that the LCP strongly reduces the viscosity of the thermoplastic matrix. In the case of blends based on Ny1, a minimum in the viscosity-composition curves was also observed. Different mechanisms have been proposed in order to account for this behavior.^{3,4,8,15,17} In general, the reduction of the viscosity has been correlated with the incompatibility of the two phases and with the reduction of the pressure drop at the inlet of the capillary. In a recent paper,²⁷ the presence of minima in the viscosity-composition curves has been correlated with particular ratios of the viscosities of the two components. In fact, these minima have commonly been

Table I Molecular Weight of Raw Materials

Sample Code	Trademark	Manufacturer	
PC1	$M_v = 36000$	Sinvet 301	Montedipe
PC2	$M_v = 20000$	Sinvet 251	Montedipe
Ny1	$M_w = 62000$	ADS 40	SNIA
Ny2	$M_w = 30000$	ASN 27	SNIA
PP1	$M_w = 680000$	D 60P	HIMONT
PP2	$M_w = 390000$	T 30S	HIMONT
LCP1	—	—	Eniricerche Hoechst-
LCP2	—	Vectra B950	Celanese

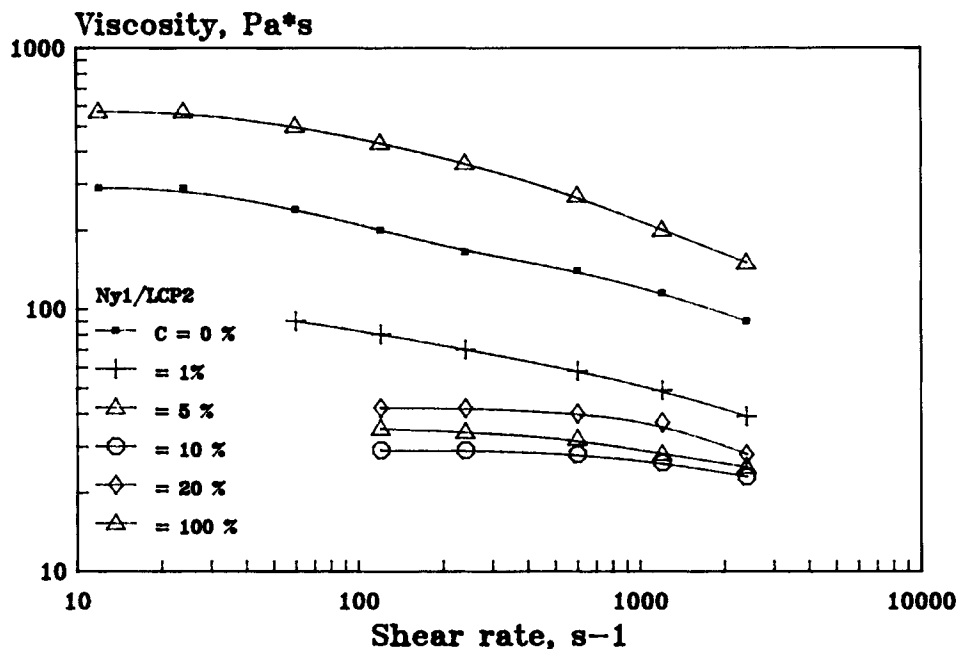


Figure 1 Flow curves of the PP1/LCP1 system at $T = 240^{\circ}\text{C}$.

observed when the viscosity of the LCP is higher than (or very close to) that of the thermoplastic polymer. This empirical rule is obeyed by all the blends described in the present paper (cf. Figs. 1-3).

A point that calls for emphasis is that this reduction of viscosity can give rise to materials with viscosity similar to that of pure injection grade materials. Thus, a high molecular weight polymer can be used not only for extrusion operations, but also

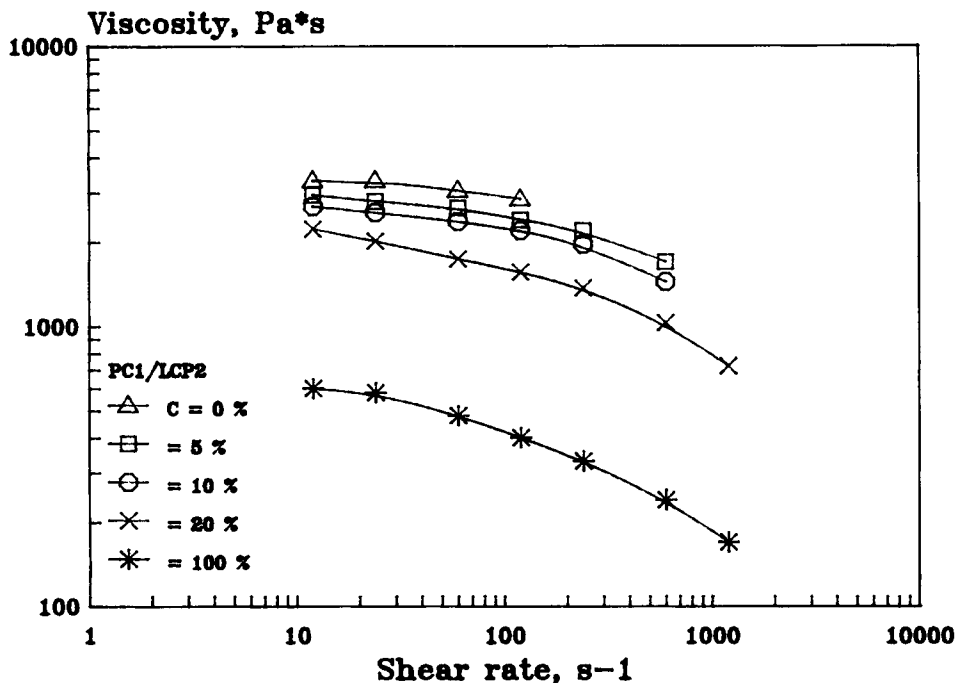


Figure 2 Flow curves of the Ny1/LCP2 system at $T = 290^{\circ}\text{C}$.

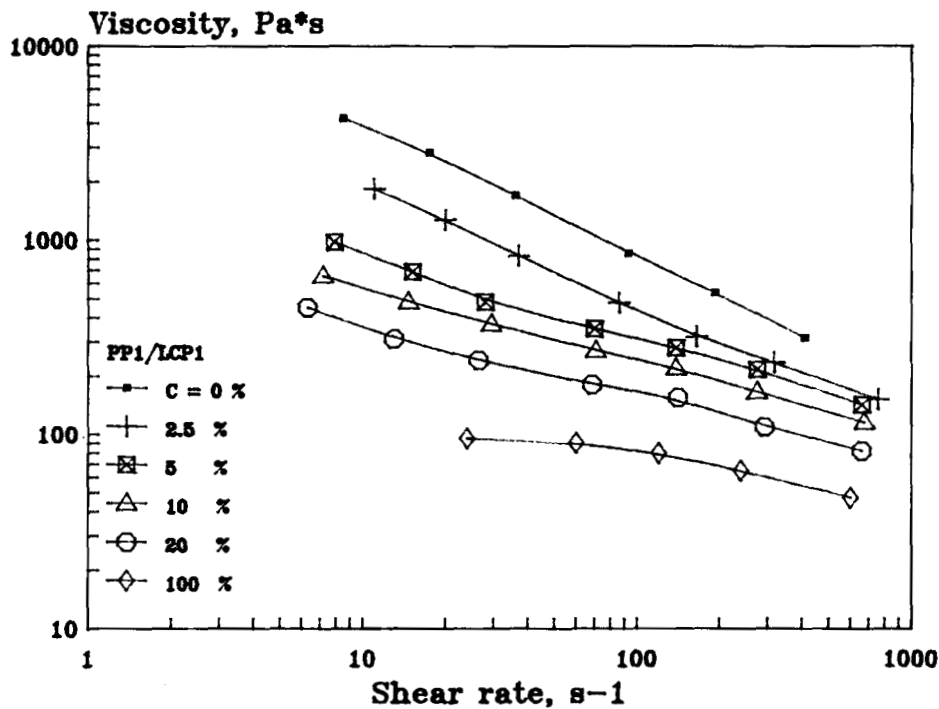


Figure 3 Flow curves of the PC1/LCP2 system at $T = 290^{\circ}\text{C}$.

for injection molding, provided that a small amount of LCP is added to it.

The dimensionless torque and the output flow rate of the extruded materials are plotted in Figures

4 and 5 as a function of the LCP content. For all the systems, the torque drastically decreases as a result of the addition of very small amounts of liquid crystal polymer to the thermoplastic materials; on

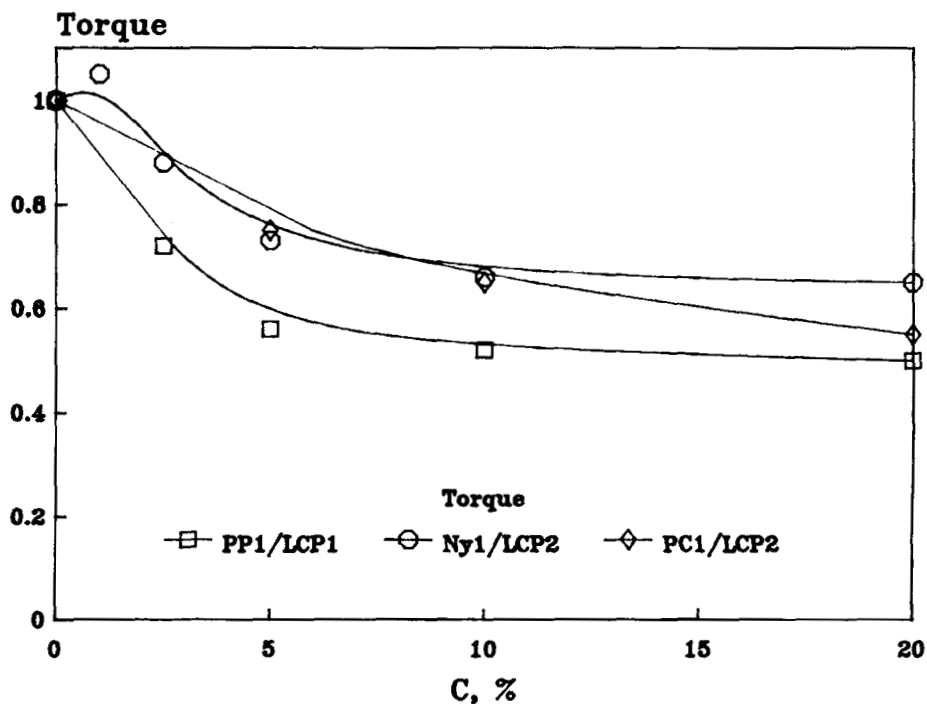


Figure 4 Dimensionless torque vs. LCP content.

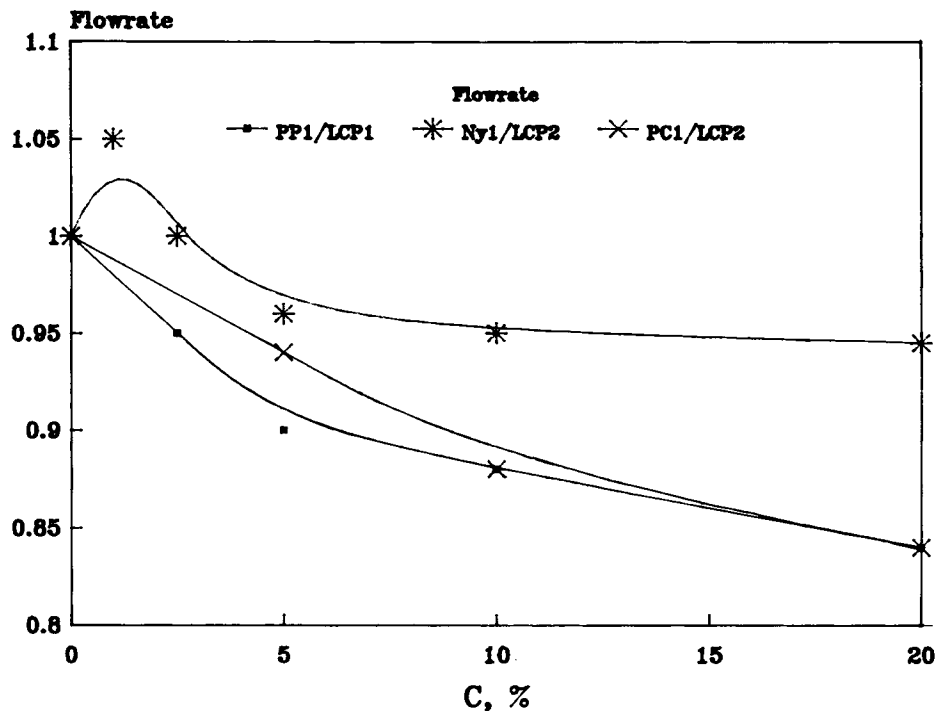


Figure 5 Dimensionless flow rate vs. LCP content.

increasing further the LCP concentration beyond 5%, the torque reduction becomes much smaller until no more change is observed at LCP contents higher than ca. 10%. As for the Ny1/LCP2 system at very low LCP content, on the contrary, a slight rise of the torque is observed.

The energy absorbed during extrusion depends on both the friction factor in the zone of transport of solids and on the viscosity in the zone of transport of melt of the extruder. However, this latter effect would imply an increase of the output flow rate, which is actually observed only at the lowest concentrations of LCP2 in the system with Ny1. In all other cases a reduction of that parameter is commonly found to occur, though to a different extent for the different blends. In order to explain this latter result, a reduction of the friction factor in the zone of the transport of solids has been invoked.¹⁶ In the system PP1/LCP1, this effect is probably less important than in the other blends. The peculiar behavior of the Ny1/LCP2 blend with $c = 1\%$ can be attributed to very low concentration of LCP which is not sufficient to reduce the friction factor in the zone of transport of solid of the extruder. In this case the dispersion of a "solid" component gives rise to an increase of the extrusion energy. Due to the high torque value and to the lower viscosity, the output flow rate increases.

Injection molding tests were performed on the blends PC1/LCP2 and PP1/LCP1. For comparison, tests on injection molding grade PC2 and PP2 were also performed. Pressure at end of filling, P_F , is plotted in Figure 6 as a function of the LCP content for both systems. As expected, both PC2 and PP2 are very easily injection-molded, whereas the corresponding extrusion grades, PC1 and PP1, can be injection-molded only with great difficulty. The data in Figure 6 show that, for blends with relatively small amounts of liquid crystal polymers, the filling pressure is very strongly reduced and becomes similar to that typical for injection grade materials. Thus, injection molding tests described above demonstrate that the addition of small amounts of LCP to extrusion grade materials makes them very easily injection moldable. Therefore, provided that the properties of the finished objects are not worsened, this practice could also allow use of these LCP-based blends of extrusion grade polymers for injection molding operations.

Among the mechanical characteristics of a polymer, impact strength appears as the most liable of worsening as a result of blending it with a liquid crystal polymer. Thus, measurements of Izod impact strength of injected specimens were carried out, and the results are reported in Figure 7 as a function of the LCP content. The data have been reproduced

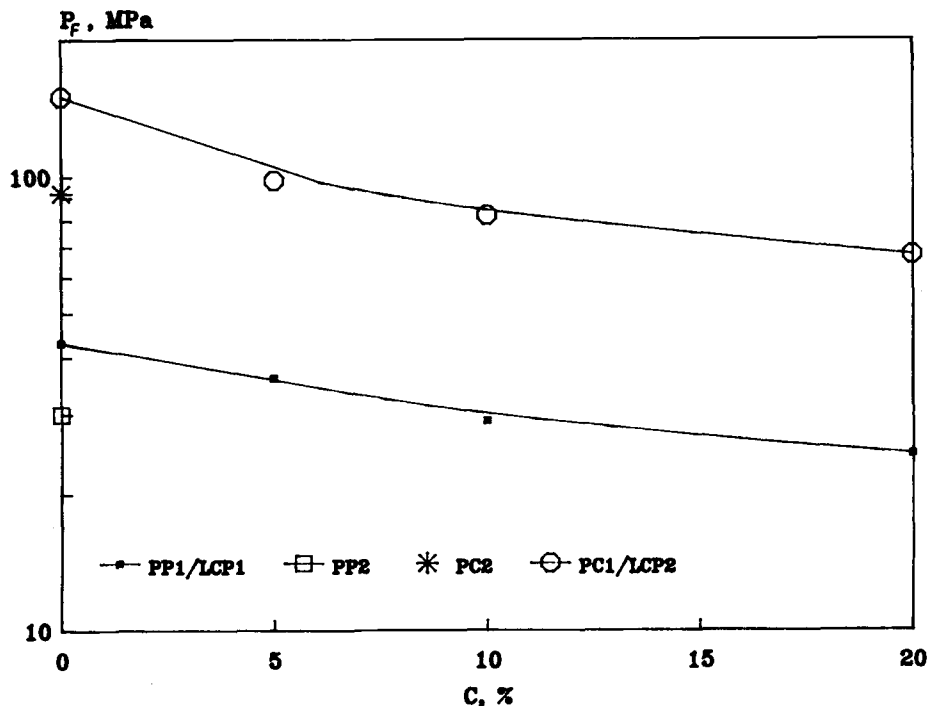


Figure 6 Pressure at the end of filling vs. LCP content.

with an error of about $\pm 5\%$ for pure polymers and slightly larger for the blends. Two different behaviors are well evident. The impact strength of the PP1/LCP1 blends goes through a small but distinct maximum, for an LCP1 content of about 5%, and then decreases progressively for larger LCP contents. On the contrary, for PC1/LCP2 blends, no

maximum is observed, although the decrease of the impact strength is very slight at low LCP contents.

However, the most interesting result of the impact tests is that the strength of the blends at low LCP content is higher than that of the corresponding injection grade material. If a blend of a low grade polymer with small amounts of LCPs is to be used as

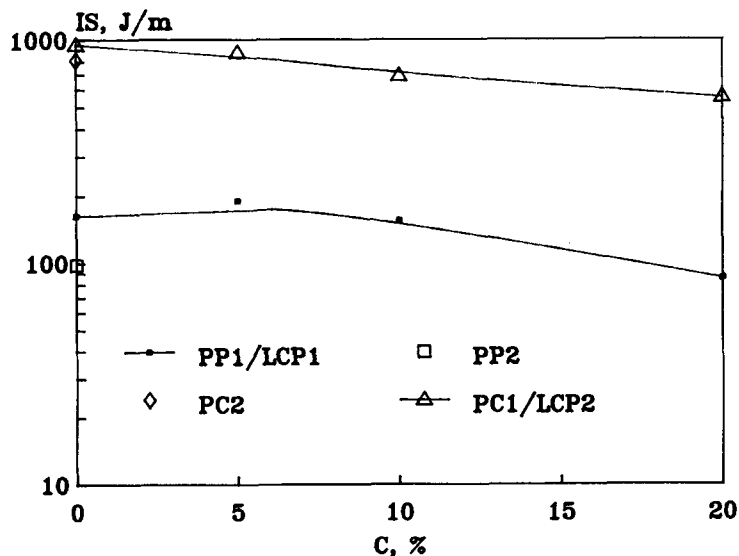


Figure 7 Impact strength vs. LCP content.

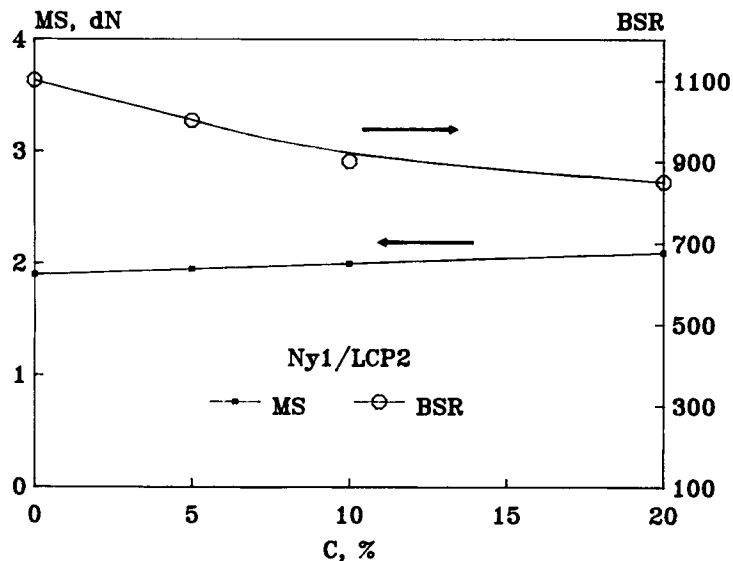


Figure 8 Melt strength and breaking stretching ratio of Ny1/LCP2 blends vs. LCP content.

“universal grade” thermoplastic, it is important to see what is the effect of blending on a processing operation, such as spinning, which requires high melt viscosity. In fact, the presence of a LCP phase has been shown to lower the melt viscosity and this might be expected to worsen the polymer spinnability.

In Figure 8 melt strength (MS) and breaking stretching ratio (BSR) values of Ny1/LCP2 blends are plotted as a function of the LCP content. It may be clearly seen that BSR decreases on increasing

the LCP content in the blends and MS is only slightly influenced by LCP. Nevertheless, both these parameters are still in the range of fully acceptable values for all the investigated compositions (up to 20% LCP). Spinning of all Ny1/LCP2 blends were in fact carried out without difficulty. The mechanical properties of the fibers obtained at different draw ratios (DR) are plotted in Figure 9. The tensile modulus of the fibers is found to increase with increasing DR and this effect is higher the higher the LCP content. In particular, the modulus of the 20%

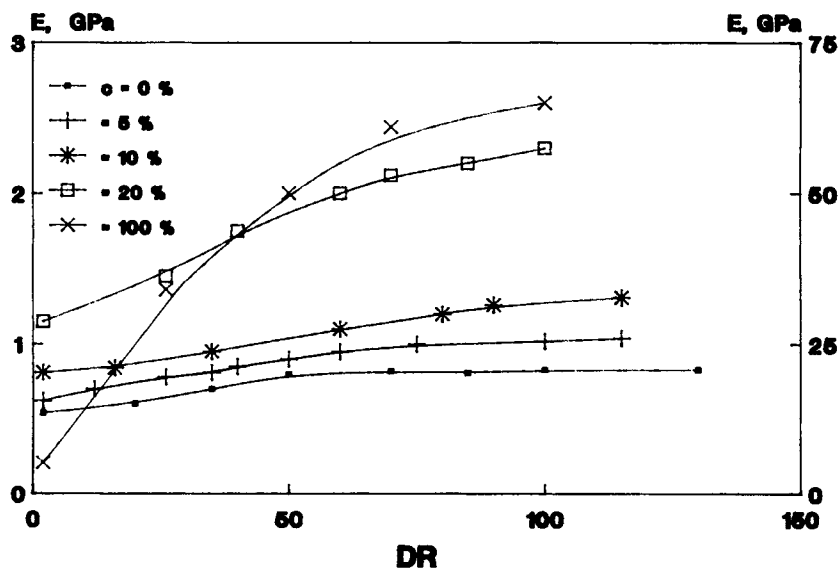


Figure 9 Elastic modulus vs. draw ratio for Ny1/LCP2 blends.

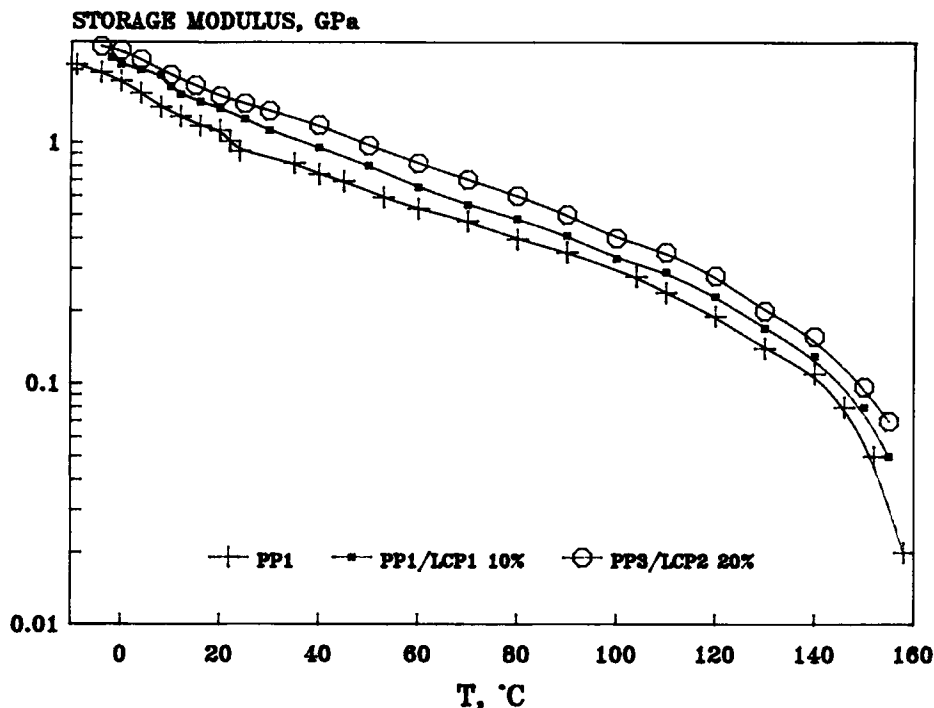


Figure 10 Storage modulus vs. temperature for PP1/LCP1 blends.

LCP fiber is about twice that of a fiber of pure Ny1. Thus, the reduced spinnability of the LCP blends is more than balanced by the improvement of the mechanical properties due to the LCP reinforcing action.

Another interesting feature of these blends is connected with the possibility to increase, in some cases, the maximum working temperature of the polymeric matrix. In Figure 10 the storage modulus of PP1/LCP1 blends and of the polypropylene is reported as a function of the temperature. It may be clearly seen that the storage modulus increases with LCP1 content. Considering the temperature at which the modulus is 0.2 GPa as the heat distortion temperature (HDT) at 66 PSI,²⁸ this value increases from 118°C for the pure matrix to 130°C for the blend with 20% LCP content. This improvement may be even larger considering HDT at larger applied stress (Table II). Of course, this increase of

Table II Heat Distortion Temperature of PP1/LCP1 Blends

Sample	HDT (66 PSI) (°C)	HDT (264 PSI) (°C)
PP1	118	44
PP1 + 5% LCP1	120	47
PP1 + 10% LCP1	125	55
PP1 + 20% LCP1	130	71

thermal resistance occurs only when the transition temperature of the LCP is larger than the glass transition temperature of the matrix.

CONCLUSIONS

The results discussed in this paper demonstrate that the blends of low grade thermoplastic polymers with small amounts of LCPs can be conveniently used for all processing operations, including injection molding. In some cases, besides preserving the good processing characteristics, the addition of the LCP has been shown to lead to appreciable improvements of the thermal and/or mechanical properties of the finished objects.

Although our analysis was restricted to a limited number of polymer/LCP blends, a review of the literature shows that similar conclusions can be drawn for other systems as well.

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