Phase Structure, Processability, and Mechanical Properties of Rodrun Liquid Crystalline 5000/Rodrun Liquid Crystalline 3000 Blends

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ABSTRACT: New liquid crystalline materials with low processing temperature, whilst maintaining the mechanical properties characteristic of the liquid crystalline polymers, were sought by blending Rodrun 5000 and Rodrun 3000. After direct injection moulding, the solid blends appeared as miscible. The crystallization from the melt was hindered by the presence of the other component, but the minimum processing temperature of Rodrun 5000 clearly decreased as a consequence of the presence of Rodrun 3000. This decrease was not at the cost of a decrease in the overall mechanical properties. It should be noted that, unlike in thermoplastics blends, in liquid crystal polymer (LCP) blends the miscibility level influences the modulus values. Immiscibility leads to clear positive synergisms in the values of the modulus of elasticity and also in the tensile strength, that are not seen in miscible LCP blends.
KEY WORDS Rodrun Liquid Crystalline 5000 / Rodrun Liquid Crystalline 3000 / Blends / Structure / Processability / Mechanical Properties /

The use of liquid crystal polymers (LCP's) as reinforcements for thermoplastic matrices has attracted considerable interest in the two last decades.[1,2] This is due to the fact that when thermoplastic/LCP blends are subjected to extensional flow, the LCP phase is deformed into fibrils that reinforce the matrix. A clear limitation of thermoplastic/LCP blends is that most of the commercial and performance LCP's have to be processed at temperatures close to 300°C. For this reason, most LCP's can be only blended with heat resistant thermoplastics. A possible solution to this problem is the reduction of the processing temperature of the LCP's by blending with another LCP with a lower processing temperature. This aspect has not been studied much;[3,4] in LCP/LCP blends, the structure,[3,5–15] rheological properties,[3,4,6,9–11,16] morphology,[6] mechanical properties[4–6,9,13,17–20] and reactions in the melt state[3,7,8,13] are the subjects of most study.

Apart from a possible reduction of the processing temperature, two additional important advantages are usually found in LCP/LCP blends: a synergistic mechanical behavior[5,6,9,13,17,19,20] and a melt viscosity lower than that of either of the pure components.[9–11] These possibilities make LCP/LCP blends clearly attractive.

Rodrun LC 5000 (R5) is an important commercial LCP with high processing temperature (300°C), whereas Rodrun LC 3000 (R3) has one of the lowest (240°C) LCP processing temperatures. Both are copolyesters of poly(hydroxybenzoic acid) (PHBA) and poly(ethylene terephthalate) (PET) with different comonomer ratios. The blends of these two LCP's could produce materials with intermediate properties that would widen the commercially available range of LCP's. This is in addition to the possibility of reducing the processing temperature of R5.

Moreover, when the phase structure of R5/R3 blends obtained in a Haake mixer was studied, the blends were found to be miscible.[14] The processability of blends of a copolymer similar to, but less random than R3 and Vectra A,[10] as well as the processability and the structure[12,16] of blends of copolymers similar to, but less random than R3 and R5 have been studied. However, neither the processability nor the mechanical properties of the blends of commercial R3 and R5 have previously been studied to our knowledge.

In this work R5/R3 blends were obtained over the full composition range by direct injection moulding. The phase structure was analysed by differential scanning calorimetry (DSC) and dynamic mechanical thermal analysis (DMTA), and the kneading torque was measured as a function of temperature to determine the decrease in the processing temperature of R5 on blending. The mechanical properties of the blends were studied by means of tensile tests.

EXPERIMENTAL

The polymers used in this work were Rodrun LC 3000 (R3) and Rodrun LC 5000 (R5) (Unitika). R3 and R5 are semiaromatic copolyesters based on poly(hydroxybenzoic acid) and poly(ethylene terephthalate) in 60/40 and 80/20 compositions, respectively.

R3 and R5 were dried before processing for 8 h at 100°C and at 135°C respectively. The dried pellets were directly melt mixed over the entire composition range in a Battenfeld BA230E reciprocating screw injection moulding machine. A melt temperature of 300°C, a mould temperature of 20°C, an injection speed of 1 cm³ s⁻¹ and an injection pressure of 2450 bar were used in the injection moulding process. The kneading torque of the pure components, and that of the 50/50 blend at 30 rpm, were measured in a Brabender plasticorder PLE

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650. The torque was measured while the melt temperature decreased from 290°C upon switching off the electrical heating.

The calorimetric analysis of the blends was carried out in a Perkin–Elmer DSC-7 calorimeter. The samples were first heated from 25°C to 320°C at 20°C min⁻¹ and subsequently cooled to 25°C at 20°C min⁻¹. The crystallization behavior of the blends and that of R3 and R5 were analysed during the cooling scan. DMTA scans from 30°C to 200°C were carried out in a Polymer Laboratories DMTA using a heating rate of 4°C min⁻¹ and a frequency of 1 Hz. Specific volume values were measured in a Mirage SD-120-L electronic densitometer with a resolution of 0.0003 cm³ g⁻¹ using butyl alcohol as the immersion liquid.

The tensile tests were carried out using an Instron 4301 at a cross-head speed of 10 mm min⁻¹ on 1.9 mm thick ASTM D-638 type IV specimens. The mechanical properties (Young's modulus (E), break stress (σ_b), and ductility, measured as the break strain (ε_b)) were determined from the load-elongation curves.

The samples (length = 20 mm) for the X-Ray diffraction measurements were cut from the central section of the tensile specimens. The X-Ray diffraction patterns of some blends were obtained using a Statton flat camera (W. H. Warhus, Co.) and Cu-K_α ($\lambda = 1.542$ Å) radiation.

RESULTS AND DISCUSSION

Phase Structure

The phase structure after direct injection moulding was first analysed by DSC. No T_g could be seen by DSC, so the T_g's of the blends were studied by DMTA. The crystallization behavior observed in the DSC scans will be discussed later.

Figure 1 shows the tan δ as a function of temperature for the pure LCP's and their blends. As can be seen, all the blends showed a single maximum in tan δ at a temperature between the T_g's of the two pure components (70 and 80°C respectively for R3 and R5). This indicates miscibility. However, taking into account the fairly close values of the T_g's of the two neat LCP's, the presence of two T_g's cannot be ruled out. Despite this, the presence of a single peak appears as probable because the transitions of the blends are not broader than those of the pure components, taking into account the composition. Moreover, the R5/R3 blends appeared as miscible after mixing in a Haake mixer.[14] Miscibility was also seen in blends of less random copolymers similar to R3 and R5,[12] and in blends of other copolymers that, as in the present work, only differed in the comonomer ratios.[3,7]

The DSC cooling scans of the pure components and of the blends are shown in Figure 2. The scans of R3 and R5 showed crystallization peaks that appeared at temperatures (T_c) of 150°C and 245°C respectively. The crystallization enthalpies (ΔH_c) were 3 and 2 J g⁻¹, respectively. The crystallization peak of R5 should be attributed to PHBA, because its T_c is too high to be that of PET.[21] Moreover, the high value (340°C) of the T_m of PHBA (22) agrees with the observed T_c. The crystallization peak of pure R3 was probably due to PET due to its low T_c. To prove this, a DSC cooling scan was carried out on neat PET under the same conditions as those for R3.
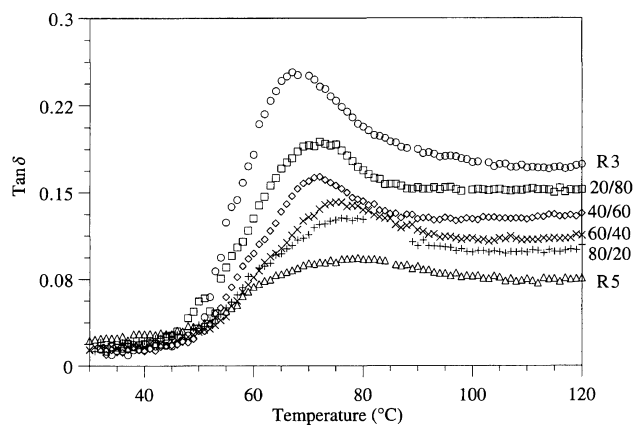

Figure 1. Tan δ vs. temperature for R5 ($\triangle$), R5/R3 80/20 ($+$), 60/40 (x), 40/60 ($\diamondsuit$), 20/80 ($\square$), and R3 ($\bigcirc$).
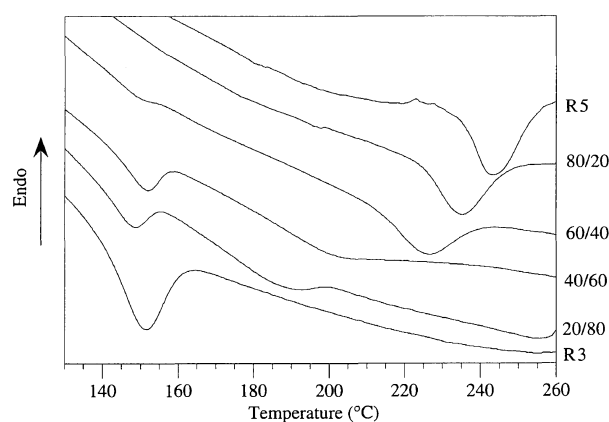

Figure 2. DSC cooling scans of the blends and of the neat components.

The observed T_c (170°C) was only slightly higher than that of R3. Therefore the T_c of R3 is due to the PET units. The slightly higher T_c of neat PET compared with that seen in R3 is due[23] to the randomness of R3.[24]

With respect to the scans of the blends (Figure 2), two crystallization peaks appeared in all the blends, with the exception of the 80/20 composition, in which only a single peak appeared. As can be seen, the low temperature T_c that corresponds to the R3 did not change with composition. However, the ΔH_c values of R3 were significantly below the calculated additive values, probably because the presence of the solid R5 hindered crystallization. In the case of the high temperature peak, the T_c decreased from 245°C to 235°C with the addition of only 20% R3, and further decreased at increasing R3 contents. The ΔH_c's were close to linearity. Thus the crystallization of R5 was also hindered by the presence of R3. The different crystallization behavior of R5 and R3 will be probably influenced by the fact that R5 crystallized from a miscibilized phase in a liquid environment, whereas the crystallization of R3 took place surrounded by a solid R5 environment. The hindered crystallization of the two components agrees with the previously mentioned miscibility.

The hindered crystallization may be due, besides to miscibility, to the occurrence of reactions between the two components. With the aim of looking for possible re-

actions, Fourier transform infrared spectrometry (FT-IR) analysis was carried out on the blends and on the pure components. The spectra of the blends and those calculated by adding the weighted spectra of the two components for each composition were almost the same. It was therefore concluded that the hindered crystallization was mainly due to miscibility.

Processability

The possibility of extending the use of the performance R5 to lower processing temperatures by means of blending it with R3 was studied by comparing the torque of kneading the melt blends in the Brabender mixer with those of the pure components. With this aim, the torque of kneading was measured at decreasing melt temperatures. These torque values are plotted against the melt temperature in Figure 3. As can be seen, the torque values of the two pure LCP's remained fairly constant below the T_m and even below the T_c (245℃ and 150℃ respectively for R5 and R3). They increased markedly indicating the minimum processing temperature only 20—30℃ below the T_c. In the case of the 50/50 blend, the behavior was similar and the torque began to clearly increase at 175℃; *i.e.*, just at the temperature predicted by the additivity rule between the values of the two pure components.

This decrease in the processing temperature at which the viscosity of the R5-based blends remains low agrees with the important T_c decrease previously observed. The observed decrease in the processing temperature of R5/R3 blends is notable because decreases clearly smaller than those predicted by the additivity rule are often obtained. Thus, although in one case,[3] the minimum processing temperature followed the additivity rule, in other cases,[12,16] the decreases (20 and 25℃) were clearly below the additive values (57 and 50℃). The minimum processing temperature was measured as a solidification temperature in ref 3, by means of the change of the complex viscosity in ref 16 and by means of the storage modulus (G') in ref 12.

Mechanical Properties

The dependence of the Young's modulus on composition is shown in Figure 4. As can be seen, the behavior of the modulus was slightly (roughly 10%) above that predicted by the additive rule of mixtures. This behavior could be due to i) a negative volume of mixing or ii) a higher orientation in the blends than in the pure components. With respect to a negative volume of mixing, the density was measured and the results plotted as specific volume in Figure 5. As can be seen, the specific volume of the blends is very close to that predicted by the rule of mixtures. In another study on free volume behavior by positron annihilation lifetime spectroscopy (PALS) on LCP blends,[14] positive deviations in the size of the free volume sites were observed in the 75/25 and 25/75 R5/R3 blends and a negative behavior in the 50/50 blends. The behavior of the number of sites was just the opposite. This behavior is difficult to compare with that observed in Figure 5. This is because, if any tendency were present, it should be a negative behavior in R5-rich blends and a positive behavior in R3-rich blends. However, information that could be related to the macroscopic free
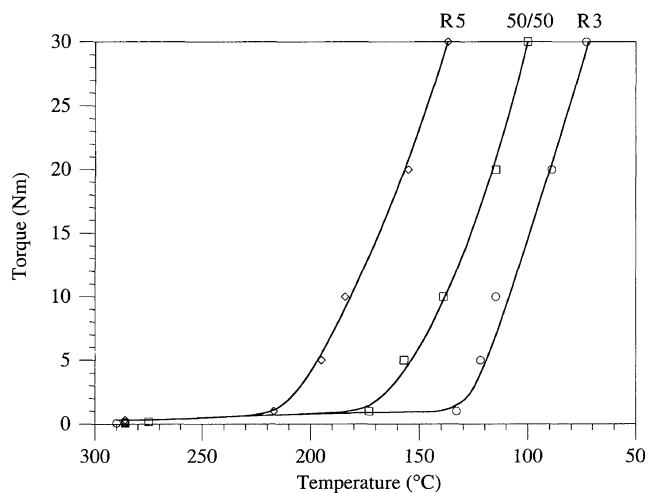

Figure 3. Torque of mixing *vs.* temperature for R5 (◇), R5/R3 50/50 blend (□), and R3 (○).
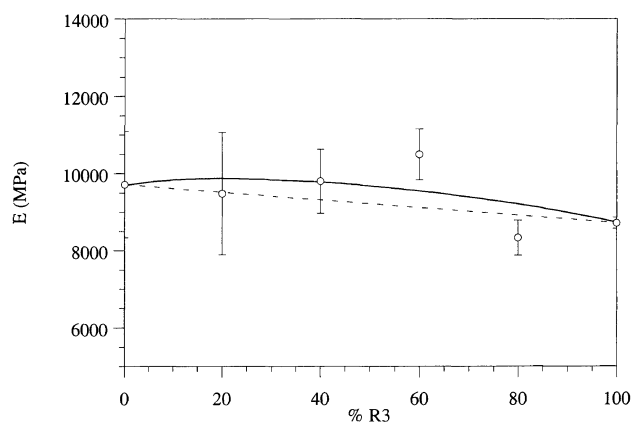

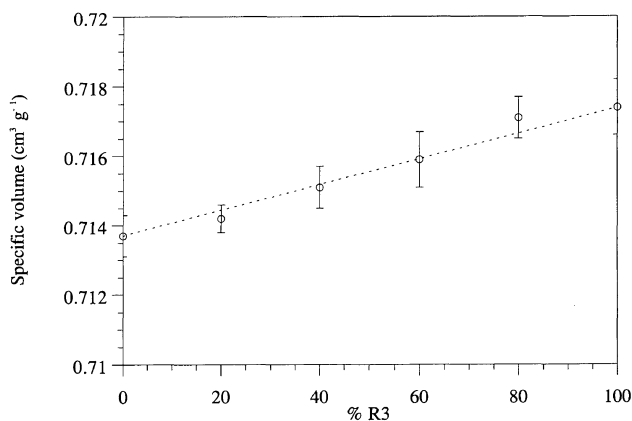**Figure 4.** Young's modulus of the blends and of the neat components *vs.* composition.

Figure 5. Specific volume of the blends and of the neat components *vs.* composition.

volume of the pure components and of each component in the blends cannot be deduced, due to the opposite behavior of the size and number of holes in the R5/R3 blends of ref 14. Moreover, neither the specific volume results of Figure 5 nor those by PALS of ref 14 agree with the modulus behavior of Figure 4. Therefore a negative volume of mixing has to be discarded as a rea-
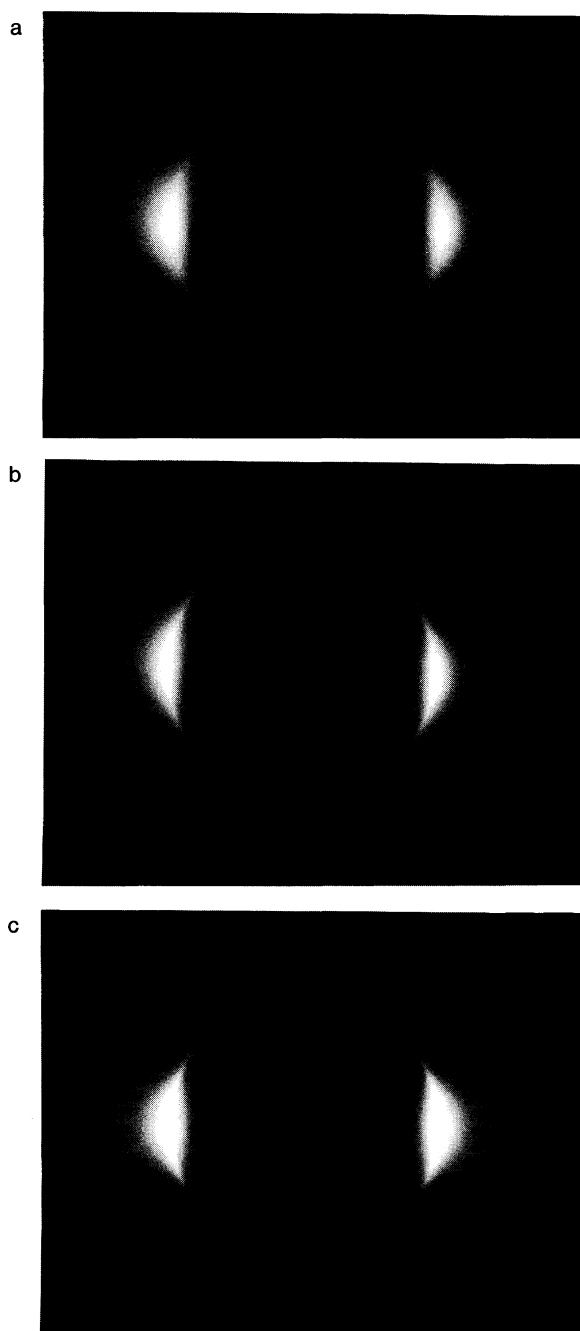
130

Figure 7. Ductility of the blends and of the neat components *vs.* composition.

Figure 6. X-Ray patterns of the (a) R3, (b) R5/R3 60/40 blend, and (c) R5.

son for the synergistic modulus behavior.

A possible difference in the orientation between the blends and the pure components was studied by X-Ray diffraction. The results are shown in Figures 6a, 6b, and 6c where the diffraction patterns of R3, the 60/40 blend and R5 respectively are shown. Some differences in the Bragg angle and the peak profile of the samples are observed. These differences are slight and do not agree with the observed modulus behavior. However, discarded specific volume effects, the orientation should be the main parameter that controls the modulus of elasticity, and synergistic modulus are often seen[5,6,9,13,20] in other LCP/LCP blends due to the increased orientation of the LCP's in the blends related to that of the pure components. Thus, the reason of the synergistic behavior
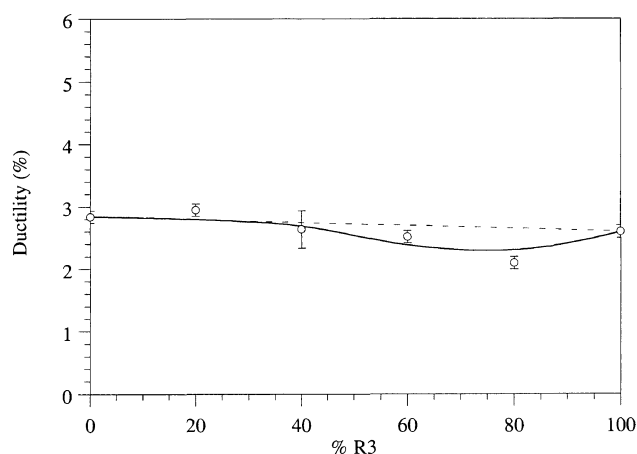
is not explained; but, despite the X-Ray results, the possibility of an orientation effect cannot be fully discarded.

The observed synergism in modulus is comparable to the 10% deviation above the additive values observed in other LCP blends,[9,17] but clearly below the 30%,[6,13] 50%[20] and even 100%[5] positive deviations also observed in other blends. Considering the reasons for these different behaviors among the unreacted blends, we realize that most of the LCP/LCP blends with large synergisms are biphasic,[6,20] and one of the blends with intermediate strength synergisms is partially miscible.[9] Finally, only very slight synergisms are observed in miscible blends. These facts suggest that, unlike thermoplastic blends, the presence of two phases is a favourable structural feature for high modulus in LCP/LCP blends. The high modulus and orientation of a biphasic blend may be due to the difference in viscosity of the components that leads to a larger orientation of the less viscous component.

Figure 7 shows the ductility of the blends *vs.* composition. As can be seen, the ductility values were almost additive. It appears that, despite the large brittleness and the differences of orientation[25] of the components, the miscibility level influences the ductility of these blends. This is because linear ductility values are seen in this work. In partially miscible blends,[9] the negative deviation is small (close to 15%) and in an immiscible blend[6] large negative deviations (40%) were observed. A patent[19] also exists, in which the miscibility suggested by the small synergism in modulus is in agreement with the nearly linear values of the ductility.

Figure 8 shows the tensile strength *vs.* composition. As can be seen, the tensile strength values are fairly additive, as was expected due to the additive ductility and only slight deviations in the modulus values. As in the case of the modulus, a biphasic nature of the blends appears to be a positive characteristic for the tensile strength. This is because immiscible blends[6] showed clear positive synergism and partially miscible blends less important synergism.[9]

CONCLUSIONS

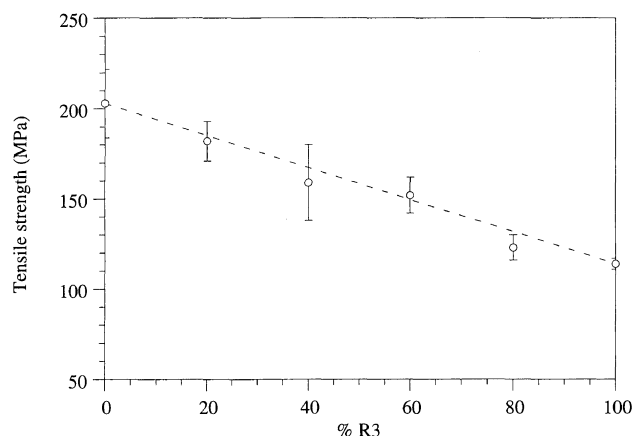Rodrun 5000 / Rodrun 3000 (R5/R3) blends are misci-

Figure 8. Tensile strength of the blends and of the neat components vs. composition.

ble after direct injection moulding, as seen by the presence in each blend of single DMTA tan δ peaks as sharp as those of the pure components. This leads to hindered crystallization of both R5 and R3. No reaction between the components of the blends could be detected by FT-IR.

The processing temperature of the R5-based blends decreases in an additive way with the addition of R3. The values of the modulus of elasticity, ductility and tensile strength of the blends were rather close to those predicted by the linear rule of mixtures with slight positive deviations in the modulus and negative ones in the ductility values. The modulus values in this and in other LCP blends, unlike thermoplastics blends, appeared to be influenced by the miscibility level, immiscibility leading to clear synergistic behavior in the modulus of elasticity. It was the same in the case of the tensile strength. In the case of ductility the usual relation in thermoplastics between miscibility and ductility levels close to additivity was, however, fulfilled.

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