

Reprocessing of Liquid-Crystal Polymers: Effects on Structure and Mechanical Properties

S. BASTIDA, J. I. EGUIAZÁBAL, and J. NAZÁBAL*

Dpto. de Ciencia y Tecnología de Polímeros, Facultad de Química, Universidad del País Vasco, P. O. Box 1072, San Sebastian, Spain

SYNOPSIS

The effects of reprocessing by successive injection molding cycles on the structure and properties of two thermotropic liquid-crystal polymers (LCPs), namely Rodrun and Vectra, were analyzed. Reprocessing produces a clear decrease in the melt viscosity of both LCPs. This is attributed to molecular weight decreases as a consequence of chemical reactions. The reactions produced chain scission in both LCPs and new products in the case of Vectra. This gave rise to modifications in the crystalline behavior of Vectra that did not take place in the case of Rodrun. All these facts lead to, with the exception of the modulus of elasticity of Rodrun, an overall decrease in properties, more marked in the case of Vectra. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

It is well known that reprocessing, which is also called primary recycling,¹ is carried out extensively in the plastics industry. It usually involves grinding the scrap from the molding processes, which is constituted mainly by faulty parts, sprues, and runners, and mixing it with virgin material in adequate proportions. The mixed recycled–virgin material is molded into new parts.

Reprocessing is interesting mainly for economic and environmental reasons. The economic interest is particularly true in the case of high-performance polymeric materials, with the high level of properties and associated price. However, reprocessing may give rise to deterioration of properties due to thermal, thermooxidative, or mechanical degradation that are mainly a consequence of the high temperatures, intensive shearing, and moisture presence during processing.

Among high-performance polymers liquid-crystal polymers (LCPs)² are characterized by a chemical structure including tractable groups that permit the formation of oriented structures in the melt state.

Thus, the degree of molecular order is intermediate between crystalline solid polymers and isotropic liquids. The dimensional order exhibited by nematic melts supposes a low viscosity in the melt, and thus LCPs are potential processing aids. Moreover, shear and elongational flows during processing of LCPs give rise to a high orientation and order in the solid state, and, consequently, although transverse properties are usually poor, to enhanced mechanical properties in the flow direction.

Exhaustive studies have been carried out on the structure, processing, and properties of most of the LCPs, as well as on their use as reinforcing second phases in blends with thermoplastics. Reprocessing of thermoplastics is the focus of much current research. However, although it has been reported recently³ that some LCPs can be reprocessed as many as five times and retain over 80% of their properties, no other studies have been published, to our knowledge, on the effect of reprocessing on the properties of LCPs.

Hence in this work we report a systematic study of the effects of reprocessing by repeated injection molding on the structure and properties of two LCPs. The possible changes of chemical structure and molecular weight because of reactions during reprocessing were tested by Fourier transform infrared (FTIR) and melt flow index (MFI). Differ-

* To whom correspondence should be addressed.

ential scanning calorimetry (DSC) was used to assess possible solid-state changes as crystalline level or perfection and mobility in the amorphous state. Structural changes at a greater scale like those observed by microscopy were also studied. The changes in the chemical as well as in the physical structure were related to the mechanical behavior of the reprocessed LCPs that was studied by tensile testing.

EXPERIMENTAL

Rodrun LC-5000 was obtained from Unitika, Tokyo, Japan. It is a copolyester with a poly(ethylene terephthalate)/*p*-hydroxybenzoic acid (18/82) composition, as determined by $^1\text{H-NMR}$. Vectra B950 was supplied by Quimidroga, Barcelona, Spain, and it is a copoly(ester-amide) based on 60/20/20 2,6-hydroxynaphthoic acid/terephthalic acid/aminophenol. Pellets of the polymers were dried before each processing cycle following the recommendations of the suppliers in order to minimize degradation reactions caused by moisture.

Injection molding was carried out in a Battenfeld BA230E reciprocating screw injection molding machine, with a screw diameter of 18 mm. The barrel temperatures were 290°C in the case of Rodrun, as used previously⁴ and 300°C in the case of Vectra. The mold temperature was 80°C in both cases. As indicated in the technical literature, high injection speeds (23 cm³/s) and low injection pressures (750 bar) were used to obtain the tensile specimens (ASTM D638, type IV). The injection parameters were the same in all the cycles. Thus, despite the fact that the nature changes as a result of reprocessing, the thermal history of the materials, taking as a reference the last solidification, was maintained constant. Samples for other experimental techniques were obtained from the injected specimens.

FTIR spectroscopy was carried out in a Nicolet 5DXC. The MFIs of Rodrun and Vectra were determined after each molding cycle with a load of 325 g and at a temperature of 290°C for Rodrun and 310°C for Vectra.

Calorimetric analysis (DSC) was performed using a Perkin-Elmer DSC-7 differential scanning calorimeter. Taking into account the complex layer structure generated during injection molding of LCPs,^{5,6} and to avoid structural differences because of the inhomogeneity in the samples, the following experimental procedure was used. The samples (approximately 15 mg), encapsulated in aluminum sample pans, were heated from 25 to 350°C at 20°C/min in order to destroy the previous thermome-

chanical history. After that, the samples were rapidly cooled down to 25°C and a second similar scan was carried out. The thermal transitions of the samples were determined in this second calorimetric scan.

Tensile tests (Instron 4301) were made at room temperature and at a crosshead speed of 10 mm/min (strain rate $2.6 \times 10^{-3} \text{ s}^{-1}$). The mechanical properties (Young's modulus E , tensile strength σ_b , and ductility ϵ_b , measured as the break strain) were determined from the load-elongation curves. A minimum of eight specimens were tested for each reported value.

RESULTS AND DISCUSSION

Structural Changes: Chemical

A first analysis of the possible chemical reactions taking place during reprocessing of Rodrun and Vectra was carried out by FTIR. In the case of Rodrun no change was observed in the FTIR spectra obtained after successive injection molding cycles with respect to that obtained for the unprocessed material. This constancy indicates that the chemical structure of the polymer does not change appreciably as a consequence of reprocessing. On the contrary, the FTIR spectra of Vectra showed several variations with reprocessing, as observed in Figure 1.

Comparing the spectrum of the unprocessed material with that of the five times processed material, some differences are evident. These differences indicate changes in the chemical structure as a consequence of chemical reactions. The most clear difference is the increase in intensity of the absorption peaks centered at 1600, 1390, 1345, 1010 and 735 cm⁻¹. Moreover, in the spectrum of the five times processed Vectra, a shoulder appears on the peak initially placed at 1140 cm⁻¹ and finally two peaks in the region from 890 to 860 cm⁻¹ appear, where a single broad peak was present in the spectrum of the unprocessed material. The chemical interpretation of these changes is usually difficult to make and is outside the scope of this work. However, in an attempt to find out if the nature of these changes was progressive or not, the material was also analyzed after the first processing cycle. As can be seen in Figure 1, most of the changes observed after five cycles are also seen after the first cycle; thus, the changes in structure take place mainly during the first processing cycle and then they are small. Thus, reprocessing of Vectra, at the level that FTIR can detect, does not give rise to new reactions but only slightly strengthens those produced in the first cycle.

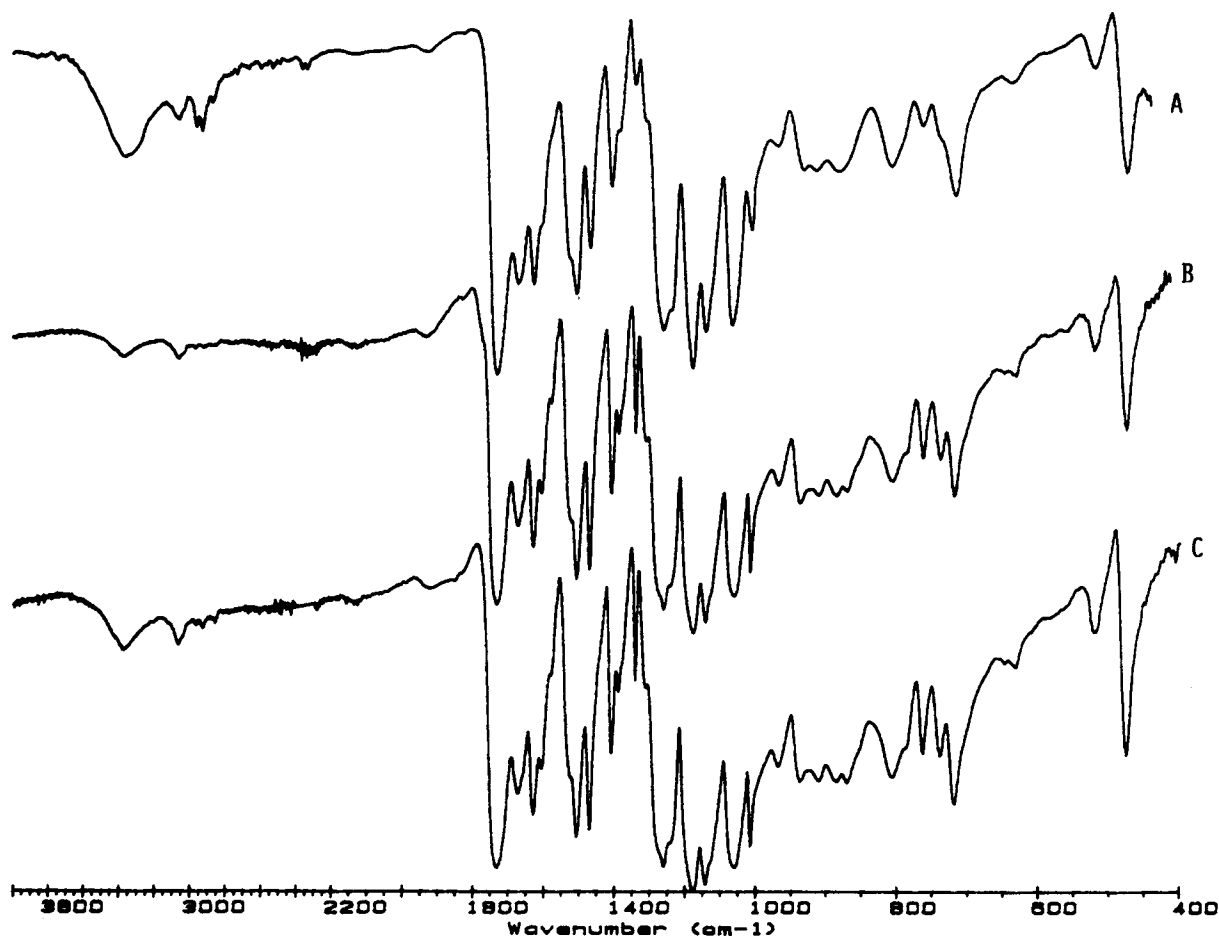


Figure 1 FTIR spectra of Vectra. (a) unprocessed material, (b) once processed material, (c) five times processed material.

Further, the extent of the reactions should be small, due to the weak intensity of the changes observed.

MFI measurements have been used in previous works⁷⁻¹¹ as a method to indirectly analyze the effects of degradation of polymers during reprocessing, among others, on the molecular weight, melt viscosity, and as a consequence, processability. The MFIs of Rodrun and Vectra are shown as a function of the number of processing cycles in Figure 2. In the case of Rodrun, a fairly continuous MFI increase was observed. In the case of Vectra, the MFI, although maintained constant after the first and second injection cycles, also increased from 30 g/10 min for the pellets to 110 g/10 min after five cycles. These increases in MFI indicate a decrease in the melt viscosity. In the case of Rodrun, given the undetected presence of new products, it must be a consequence of a decrease in molecular weight due to reprocessing. In the case of Vectra, the increase in MFI also indicates a molecular weight decrease, but the

changes in chemical structure may also play a role in the observed behavior.

In conclusion, FTIR and MFI results indicate that degradation reactions occur during reprocessing of both LCPs. They lead to a decrease in molecular weight of the two LCPs. In the case of Rodrun, no chemical structural changes are detected, whereas in Vectra chemical reactions are evident.

Structural Changes: Solid State

Calorimetric analysis by means of the change in thermal properties gave useful indications of the effects of reprocessing on the solid-state structure of Rodrun and Vectra. In the case of the unprocessed Rodrun, a glass transition was observed at approximately 58–59°C. A similar transition was observed by Wunderlich et al.¹² for a 20/80 poly(ethylene terephthalate-co-*p*-oxybenzoate) copolymer at a higher temperature and was attributed to the eth-

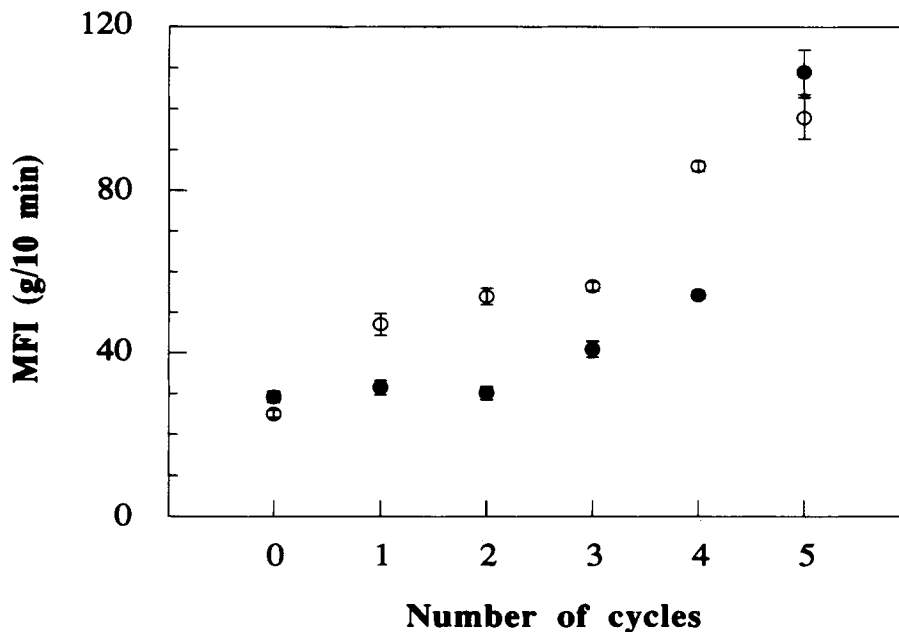


Figure 2 Effect of reprocessing on the MFI of (○) Rodrun and (●) Vectra.

ylene-terephthalate-rich phase of the copolymer. The difference in temperature was found because the T_g determined by Wunderlich et al. was measured at the point where half the increase in heat capacity had occurred, and in this work it was measured at the onset of the transition. A second wide glass transition seemed to appear in Rodrun at approximately 150°C. It could be related to that observed by Wunderlich et al. at 180–185°C, that was attributed to a *p*-oxybenzoate-rich phase.

Both of the transitions at 59 and 150°C were unaffected by reprocessing and by the consequent decrease in molecular weight. These results agree with the great but not drastic MFI increase, because it is known¹³ that in high polymers, the effect of molecular weight on glass transition temperature is seen only when very low molecular weights are attained.

With respect to the melting of Rodrun, a melting endotherm was seen with a T_m of 280°C measured at the maximum and a melting heat of 3.6 J/g. This thermal behavior is similar to that of the copolymer studied by Wunderlich et al.¹² Thus, despite the fact that that LCP was believed to have a fairly block structure, whereas that of Rodrun is considered random,¹⁴ both materials show similar thermal behavior.

After reprocessing, no significant variation of the T_m was observed, because the maximum was placed at temperatures between 275 and 280°C. The heat of melting was also practically unaffected by reprocessing, and the differences between

the extreme values, 3.4 and 3.8 J/g, were attributable to the experimental error, mainly in drawing the baseline of the endotherms. Thus, calorimetric results showed that, in spite of the molecular weight decrease as a consequence of reprocessing, the thermal behavior of Rodrun, and consequently the solid-state main features of both of its phases, were unaffected.

In the case of Vectra, the thermal behavior was characterized by a glass transition and a melting endotherm. The glass transition was placed at approximately 120°C in the unprocessed material. This value agrees with the $T_g = 137.5^\circ\text{C}$ determined by dynamic-mechanical analysis (DMTA),¹⁵ as it is known that glass transition temperatures determined by DMTA are usually higher than those measured by DSC. The glass transition temperature of Vectra, as in the case of Rodrun, almost did not change (only 2–3°) because of reprocessing, but the transition showed a greater intensity and appeared thinner the greater the number of processing cycles.

In Table I, the melting temperatures and heats obtained after each processing cycle are reported. The melting temperature for the unprocessed material was 284.9°C and the melting heat was 4.4 J/g. These values agree with those reported in the literature¹⁶ that are $T_m = 290^\circ\text{C}$ and $\Delta H_m = 3.2$ J/g. These differences are attributed to the well-known dependence on the thermomechanical history of the crystalline nature of polymeric materials, including LCPs.

Table I Melting Data for Reprocessed VECTRA B950

Number of Processing Cycles	T_m ($^{\circ}\text{C}$)	ΔH_m (J/g)
0 (Virgin material)	284.9	4.4
1	282.4	4.2
2	281.8	3.5
3	275.2	3.2
4	272.5	3.1
5	270.8	3.4

As is observed in Table I, both the melting temperature and the melting heat of Vectra decreased as a consequence of successive injection molding cycles. These changes took place in spite of the fact that the thermomechanical history^{17,18} after melting is the same for all the samples studied. Thus, the observed changes, although slight, agree with the change of nature and appearance of new products in the case of Vectra.

Thus, in summary, these facts indicate a greater "amorphous character" of Vectra and a narrower scatter of mobility in its amorphous solid state. These results also indicate a decrease in the crystallization ability of the polymer, and also the poorer crystals obtained as a result of reprocessing.

Mechanical Properties

The reported effects of reprocessing on the structure of Rodrun and Vectra have consequences for their mechanical properties. All the materials showed the typical rigid-brittle behavior, fully linear-elastic in the case of Vectra, and in the case of Rodrun linear-elastic in the first half of the curve with a posterior slight slope decrease. The topography of the broken surfaces did not change as a result of reprocessing.

In Figure 3, the Young's modulus against number of processing cycles for both Rodrun and Vectra are shown. In the case of Rodrun a practically constant value of 11,500 MPa is obtained for this small-strain property. No values of the tensile modulus of Rodrun were found in the literature for comparative purposes, but this high value agrees with that expected for an LCP and is somewhat higher than the reported flexural modulus.¹⁴ The constancy of the Young's modulus with reprocessing indicates, taking into account the lack of change of nature of the LCP and the constancy of the crystallinity level, that the observed decrease in molecular weight does not affect this property. This constancy in Young's modulus is usual when reprocessing of thermoplastic polymers is carried out.¹⁹ However, an effect of reprocessing on the Young's modulus of LCPs would be expected as a consequence of the variation of melt viscosity. It has been reported by Jackson and

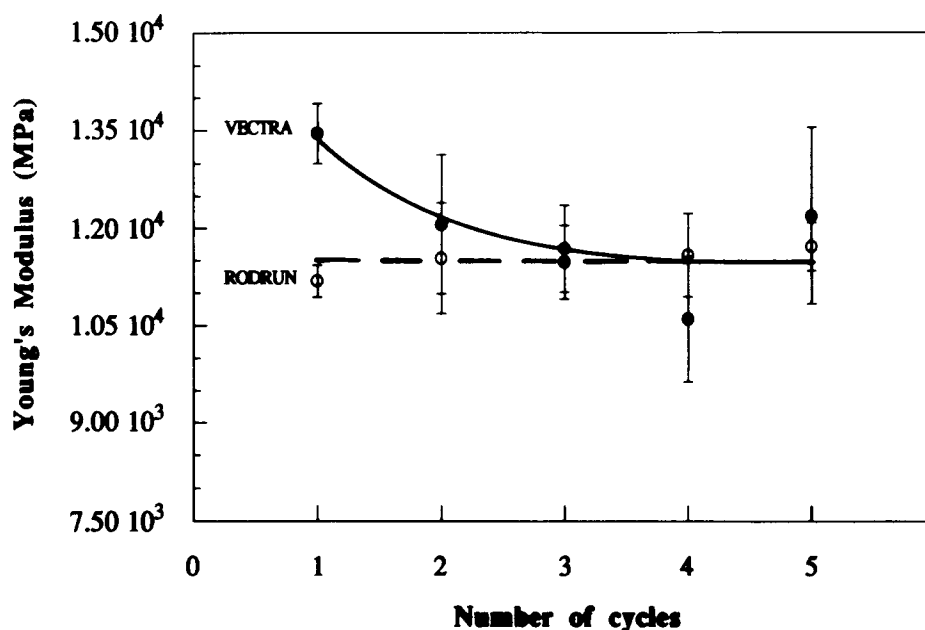


Figure 3 Effect of reprocessing on the Young's modulus of Rodrun and Vectra. Symbols as in Figure 2.

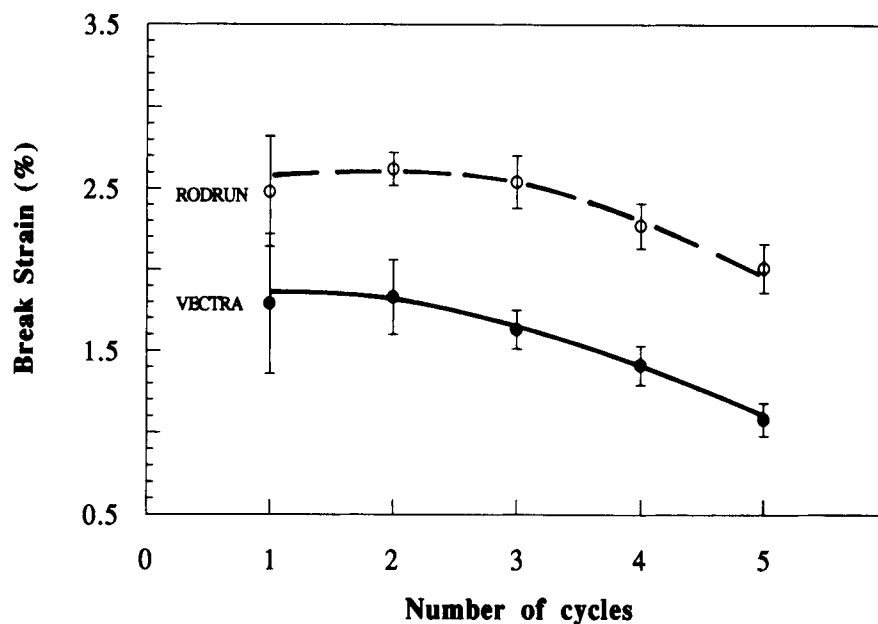


Figure 4 Effect of reprocessing on the break strain of Rodrun and Vectra. Symbols as in Figure 2.

Kuhfuss²⁰ that an increase in intrinsic viscosity (and, consequently, in melt viscosity) of a LCP gives rise to an increase in stiffness and strength. On the other hand, it was found in the same work that an increase in melt temperature gave rise to an increase in mechanical properties. This increase was attributed to a decreased melt viscosity and a concomitant increase in orientation. Thus, the effect of melt viscosity on orientation and hence on mechanical properties of LCPs is not clear. In any case, and given the variation of MFI and Young's modulus of Rodrun with the number of processing cycles, it appears that melt viscosity does not affect the orientation level attained by Rodrun.

In the case of Vectra, the Young's modulus obtained for the material after the first processing cycle was approximately 13,500 MPa. This value is lower than that reported in the Hoechst's literature, which is 19,300 MPa. This is probably due to different processing conditions, and therefore different orientation levels attained in both works. As a consequence of reprocessing, the Young's modulus of Vectra shows, taking into account its usually good reproducibility, a surprising overall tendency to decrease as the number of processing cycles increases. The changes observed in the amorphous state cannot be relevant for mechanical properties. Thus, it appears that the structural changes detected by FTIR coupled with the molecular weight and crystallinity decrease are responsible for the Young's modulus decrease.

If we try to find out the relative importance of each of the former parameters, with respect to molecular weight, the change of MFI was almost opposite to that of modulus, because it changed mainly after several processing cycles. Thus, the decrease in modulus seems to be due to either of the two other possibilities. It was observed that the greatest modulus decrease takes place in the second molding cycle. The FTIR spectra did not change very much between the first and second or even third processing cycles. However, the greatest decrease in melting heat takes place between the first and the second molding cycles. This makes the changes in crystallinity in Vectra B950 as a result of reprocessing the main parameter determining the modulus decrease despite the rather low crystallinity levels and their changes. This is an unexpected result because, contrary to the behavior of most polymers, crystallinity level would not play such an important part in the modulus of elasticity, that ought to be a direct consequence of the orientation level attained.

In Figure 4, the variation of the break strain with the number of injection molding cycles is shown. The importance of ductility is smaller in LCPs than in other polymers for engineering applications,²¹ but it plays an important role in such an important property as tensile strength, due to the shape of the tensile curves. As is observed, and as is typical in LCPs, the break strain of both LCPs is very small. In both cases the break strain remains essentially constant up to the third processing cycle and then

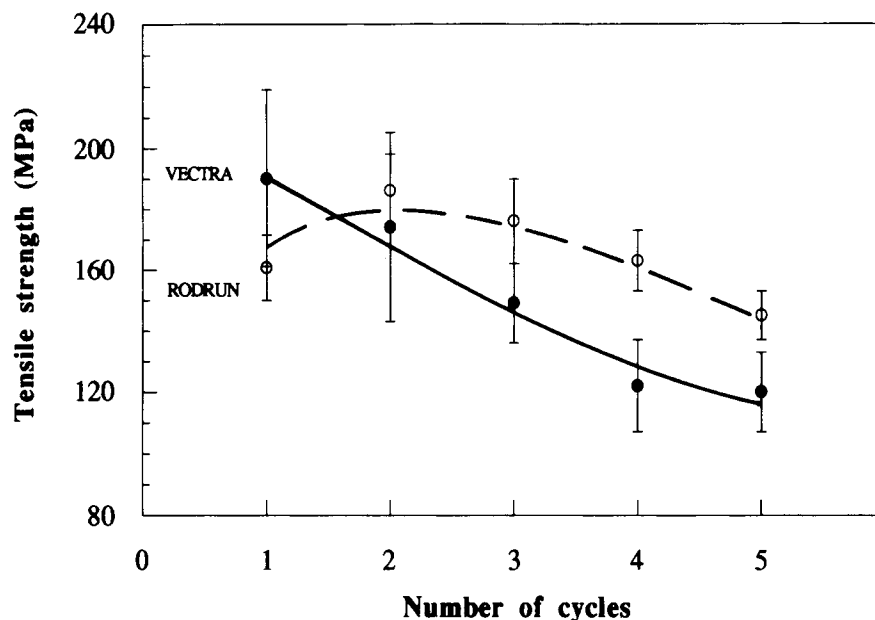


Figure 5 Effect of reprocessing on the tensile strength of Rodrun and Vectra. Symbols as in Figure 2.

decreases. Considering the reasons for these behaviors, in the case of Rodrun, the only change observed with reprocessing was the MFI increase, so that the decrease in molecular weight that this indicates seems to be the reason for the observed ductility decrease. In the case of Vectra, the increase in MFI was accompanied by a change in nature and a small crystallinity decrease. The crystallinity decrease should have, if any, an opposite influence, and the change in nature took place mainly in the first cycle, so that the change in molecular weight seems to be the reason for the observed ductility decrease.

In Figure 5, the tensile strength of the LCPs is shown against the number of processing cycles. Given the linear shape of the curve of Vectra, and the almost linear shape of that of Rodrun, tensile strength is, in both cases, a direct consequence of both ductility and modulus. Thus, in the case of Rodrun the constancy of the modulus of elasticity with reprocessing gives rise to rather similar ductility and tensile strength plots. In the case of Vectra, its continuous tensile strength decrease seems to be a consequence of the decrease in modulus in the second and third cycles, and that in ductility after successive cycles.

CONCLUSIONS

Reprocessing affects the structure of both Rodrun and Vectra. In Rodrun, a decrease in molecular

weight, probably due to chain scission, is found. In the case of Vectra, the molecular weight decrease is accompanied by the appearance of new chemical structures. Similarly, the solid-state structure did not change after reprocessing in the case of Rodrun, but it did in the case of Vectra, giving rise to a less perfect crystalline network and to a less crystalline polymer.

In the case of Rodrun, the decrease in molecular weight does not change the modulus of elasticity. However, ductility and consequently tensile strength decrease after the third cycle. The additional change of crystallinity that takes place in Vectra gives rise to a decrease in modulus of elasticity that, concomitant with the ductility decrease, gives rise to a decrease of 37% with respect to the original value in the tensile strength of Vectra after a very harsh reprocessing of five injection molding cycles.

The financial support of the Spanish Comisión Interministerial de Ciencia y Tecnología (Project number MAT92-0826) is gratefully acknowledged. One of us (S.B.) acknowledges the Basque Government for the award of a grant for the development of this work.

REFERENCES

1. J. Leidner, *Plastics Waste, Recovery of Economic Value*, Marcel Dekker, New York, 1981.

2. E. Baer and A. Moet, Eds., *High Performance Polymers*, Hanser, New York, 1991.
3. A. Stuart, *Mod. Plast. Int.*, January 27 (1992).
4. J.-I. Suenaga, *Polym. News*, **15**, 201 (1990).
5. H. Thapar and M. J. Bevis, *Plast. Rubb. Proc. Appl.*, **12**, 39 (1989).
6. C. M. Hsiung, J. Tian, and M. Cakmak, *Int. Polym. Process.*, **8**, 164 (1993).
7. J. I. Eguiazábal and J. Nazábal, *Eur. Polym. J.*, **25**, 891 (1989).
8. J. I. Eguiazábal and J. Nazábal, *Polym. Eng. Sci.*, **30**, 527 (1990).
9. A. Arzak, J. I. Eguiazábal, and J. Nazábal, *Plast. Rubb. Comp. Proc. Appl.*, **15**, 119 (1991).
10. P. Sanchez, P. M. Remiro, and J. Nazábal, *Polym. Eng. Sci.*, **32**, 861 (1992).
11. A. Ram and S. Getz, *J. Appl. Polym. Sci.*, **29**, 2501 (1984).
12. W. Meesiri, J. Menczel, U. Gaur, and B. Wunderlich, *J. Polym. Sci., Polym. Phys. Ed.*, **20**, 719 (1982).
13. L. H. Sperling, *Introduction to Physical Polymer Science*, Wiley, New York, 1986, p. 273.
14. J.-I. Suenaga and T. Okada, *Mol. Cryst. Liq. Cryst.*, **169**, 97 (1989).
15. A. Zaldua, Ph.D. Thesis, University of the Basque Country, San Sebastian, Spain (1993).
16. L. I. Minkova, M. Paci, M. Pracella, and P. Magagnini, *Polym. Eng. Sci.*, **32**, 57 (1992).
17. J. Sarlin and P. Törmälä, *J. Appl. Polym. Sci.*, **50**, 1225 (1993).
18. Y. J. Lee and S. C. Kim, *Polym. Adv. Technol.*, **5**, 374 (1993).
19. J. I. Eguiazábal and J. Nazábal, in *Handbook of Advanced Materials Testing*, N. P. Cheremisinoff, Ed., Marcel Dekker, New York, 1995, p. 871.
20. W. J. Jackson, Jr., and H. F. Kuhfuss, *J. Polym. Sci., Polym. Chem. Ed.*, **8**, 2043 (1976).
21. G. Kiss, *Polym. Eng. Sci.*, **27**, 410 (1987).

Received June 15, 1994

Accepted January 8, 1995