Crystallization and Compatibilization of Polypropylene–Liquid Crystalline Polyester Blends

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ABSTRACT: A liquid crystalline polyester, LC3000, has been blended with polypropylene. These polymers form an incompatible and immiscible blend. Polypropylene grafted with epoxy via glycidyl methacrylate forms an effective compatibilizer. The dispersed liquid crystalline polyester particle size was decreased when the compatibilizer was used. The polyester influenced the morphology of the polypropylene continuous phase by increasing the nucleation, and the effect was enhanced when the compatibilizer was present. This was demonstrated using continuous cooling DSC where the crystallization temperatures were increased. Isothermal crystallization showed decreased crystallization half-times with the polyester present, and these were further reduced with compatibilizer. Avrami analysis showed that the exponent values increased by an average of 0.1–0.2, so nucleation was assisted by the LC3000, and the rate coefficients were increased. The continuous cooling and isothermal DSC measurements provided complementary results. Optical microscopy showed that the spherulite size of the polypropylene was reduced. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 77: 2229–2236, 2000

Key words: liquid crystalline polymer; polypropylene; polymer blend; morphology; crystallization; compatibilizer

INTRODUCTION

Main chain Liquid Crystalline Polymers (LCPs) have been used in thermoplastic blends in recent times both to enhance processability (reduce viscosity) and to provide *in situ* reinforcement.[1] This arises due to the tendency of low-viscosity main-chain LCPs to readily fibrillate, particularly when deformed in an extensional flow field. However, because most main-chain LCPs are copolyesters, they are polar, and contain rigid aromatic groups, and thus the interfacial tension between them is high[2] and they are both immiscible and poorly adhering in the solid state.

Polypropylene (PP) properties can be significantly enhanced by fillers such as glass and carbon fibers, and thus make it a good candidate for fibrillar reinforcement by LCPs, while in recent studies the PP has been blended at the temperatures (280 to 290°C) required for LCP processing,[3] and novel technologies have been developed that readily allow for materials to be combined downstream after being melted at their respective processing temperatures.[4]

While the LCP fibrils may increase the modulus of the composites, particularly in the flow direction, interfacial adhesion and properties in the direction perpendicular to flow and impact strength are poor. However, grafted PPs with maleate or glycidyl functionality are now becoming readily available or reactively synthesized in-house. The grafts involving maleic anhydride (PP-*g*-MA) or epoxy (glycidyl methacrylate) (PP-*g*-GMA) groups can potentially react or become involved in hydrogen bonding with hydroxy or carboxy on the LCP polyester and provide compatibilization between the phases. The compatibilization of LCPs has lagged somewhat behind that of other immiscible blends, and where it has occurred, it has been predominantly (but not exclusively) involved blends with PP.

Some of the results reported to date have spanned both the key LCPs and the major PP-grafted materials. The LCPs investigated to date are Vectra A950 [23 mol % hydroxybenzoic acid (HBA) and 77% hydroxy-napthoic acid (HNA)], Vectra B950 [58 mol % HNA, 21 mol % terephthalic acid (TA) and 21 mol % hydroxyacetanilide (HAA)], and Rodrun LC3000 [60 mol % HBA and 40 mol % ethylene terephthalate (PET)]. Vectra A950 and B950 are rigid-chain copolyesters produced by Hoechst-Celanese, whereas Rodrun LC3000 is a semiflexible LCP produced by the Unitika Corporation. Vectra A950 and PP blends were found to have their tensile properties improved by addition of PP-*g*-MA, although impact strength was not much increased[3] with the range of anhydride compositions and compatibilizer concentrations tested—the optimum being 5% (mass) compatibilizer and 0.4% (mass) anhydride units. In general, PP-*g*-MA improved the fineness of the dispersion and improved compatibility. Improved impact properties were also found when PP-*g*-MA was added to blends of PP with the other rigid-chain copolyester, Vectra B950,[5] possibly due to the more polar HAA group found in this LCP. Even so, it was shown that the interaction in this blend was largely physical rather than a chemical reaction.[6]

Similar improvements were found with PP-*g*-MA and semiflexible Rodrun LC3000 with tensile properties such as modulus and strength showing a positive deviation from the rule of mixtures, although it was clear from this study (O'Donnell and Baird[6]) that the type of LCP was important. More recent work has involved use of PP-*g*-GMA in blends with Vectra A950 and PP,[7]

where a finer LCP morphology was obtained, and particle size decreased from 2–3 μm to 0.5 μm, although less fibers were formed. PP grafted with acrylic acid has been used as a compatibilizer for an LCP-containing sebacic acid, 4,4′-dihydroxybiphenyl and 4-hydroxybenzoic acid.[8] The potential problem of decreasing interfacial tension by addition of a third component is that the finer dispersion may be less fibrillar and thus less reinforcing, although most of the above research indicates that this is counteracted somewhat by improved adhesion.

However, polypropylene depends not only on added reinforcements for its properties but also on its crystallinity and spherulite size. Added components can provide nucleation at the interface, increase nucleation in the bulk by contributing nuclei, or decrease nucleation by absorbing nuclei. These processes are like an extraction where a species will be distributed between two phases. Thus, the effect of a dispersed phase in polypropylene may be much different from that expected from additivity. This has been highlighted by recent LCP–PP blend research by Choi et al.,[9] where an *in situ* produced compatibilizer between PP and ethylene–glycidyl methacrylate reduced the amount of PP crystallinity, even though the addition of the LCP phase had itself increased it. Such lower crystallinity can lead to a reduction in modulus.

Blends of LCPs have been formed with other thermoplastics. Vectra 950 has been blended with poly(phenylene sulfide) (PPS) and the Vectra formed immiscible droplets. The shear viscosity of the blends was increased by the Vectra, although the pure Vectra had the highest viscosity.[10] Blends were also investigated with PPS, PP, and Vectra.[11] Poly(butylene terephthalate) (PBT) has been blended with a liquid crystalline polyester of poly(ethylene terephthalate-*co-p*-oxybenzoate) (PHB), and the crystallization rate of the PBT was found to decrease with lower crystallization temperatures upon continuous cooling.[12] Poly-(ethylene terephthalate) (PET) has also been blended with a PHB, and the crystallization rate has been found to increase with the PHB acting as a nucleating agent for the PET. The crystallization rate of the PET was also increased by increased blending time, because a more uniform blend was obtained.[13] Blends of PET with a LCP consisting of butylene terephthalate and 4-hydroxybenzoate have been prepared by both solution and melt-blending methods. The blends were
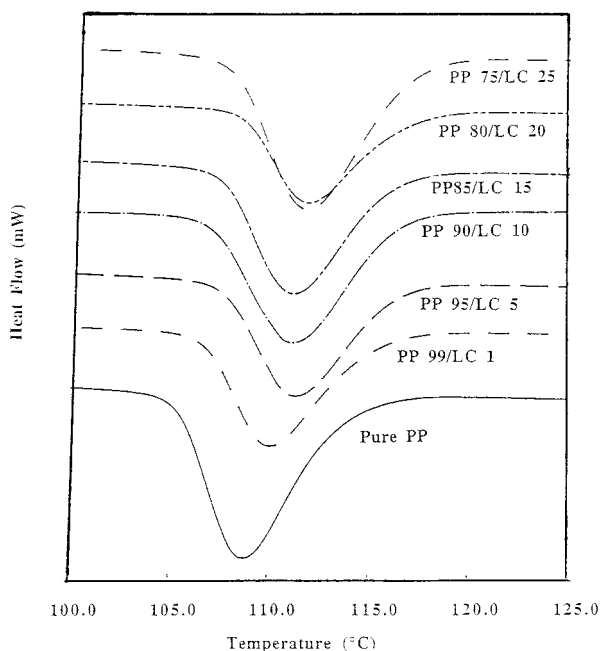
Figure 1 DSC curves of different PP–LCP blends crystallized under 10°C/min cooling rate.

shown to be immiscible, but with significant interactions, which led to a different nucleation mechanism compared to that in the PET–Vectra blends.[14]

In this study polypropylene has been blended with a liquid crystalline polyester with and without a glycidyl methacrylate-grafted polypropylene compatibilizer. The morphology of the polypropylene phase has been studied by characterization of crystallization and melting using both differential scanning calorimetry and optical micros-

copy. Little research has been done to date on the effect of LCP on PP crystallinity in their binary or compatibilized blends. A significant body of research does exist on binary blends of various LCPs and other semicrystalline matrices such as PET, and this has been summarized elsewhere recently.[9]

EXPERIMENTAL

Polypropylene (PP) was supplied by Himont, with a molar mass, $M_w = 590{,}000$ and $M_n = 111{,}948$ g/mol (polydispersity = 5.4) and was blended with the LCP Rodrun LC3000 (LC3000 chemical composition stated above) using a Brabender static mixing head at 250°C under nitrogen for 5 min, and the extrudate was ground to a powder. Blends were prepared with 5, 10, 15, 20, and 25% (mass) LC3000. The 20% (mass) LC3000 blend was compatibilized with an Eastman Chemical Company PP-g-GMA polymer ($M_w = 136{,}028$, $M_n = 51{,}609$ g/mol, polydispersity = 2.63 and glycidyl methacrylate content of 1.5%) at levels of 1, 2, 5, and 10% (mass) loadings. Previous studies have shown that binary blends of PP and LC3000 are clearly immiscible.[6]

Differential scanning calorimetry (DSC) was performed on samples of about 4 mg using a Perkin-Elmer DSC7. Samples were heated to 200°C for 2 min, and then cooled at 10°C/min to 40°C, then heated at 10°C/min to 200°C. The degree of crystallinity (X) was calculated from:

$$X = \Delta H/\Delta H_f \qquad (1)$$

Table I **Crystallization Temperature (T_c) and Heat of Fusion (ΔH) of PP in Various Blends under 10°C/min Cooling Rate**

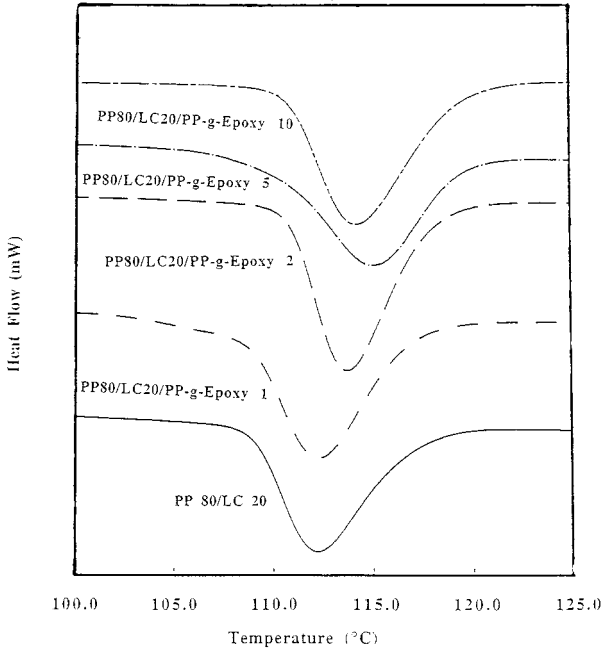| No.	Samples	Mass (mg)	T_c (°C)	ΔH (J/g)
1	Pure PP	4.17	108.97	89.98
2	PP 99/LC 1	3.98	110.15	90.04
3	PP 95/LC 5	3.09	111.48	91.37
4	PP 90/LC 10	3.84	111.40	92.75
5	PP 85/LC 15	4.23	111.35	93.94
6	PP 80/LC 20	4.54	112.18	92.33
7	PP 75/LC 25	4.41	112.15	92.59
8	PP80/LC20/PP-g-Epoxy 1	4.52	112.20	91.75
9	PP80/LC20/PP-g-Epoxy 2	4.27	113.65	95.50
10	PP80/LC20/PP-g-Epoxy 5	4.90	114.90	95.59
11	PP80/LC20/PP-g-Epoxy 10	4.25	114.10	96.16

Figure 2 Effect of compatibilizer (PP-*g*-epoxy) on the crystallization of PP 80–LCP 20 blend under 10°C/min cooling rate.

where ΔH is the heat of fusion per gram of PP measured from the nonisothermal scan, and ΔH_f is the heat of fusion of 100% crystalline PP. The ΔH_f used in this calculation was 180 J/g.

Isothermal crystallization was measured by heating the sample to 180°C for 2 min, followed by cooling at 100°C/min to the chosen isothermal temperature. Isothermal DSC data was analyzed using the Avrami equation:
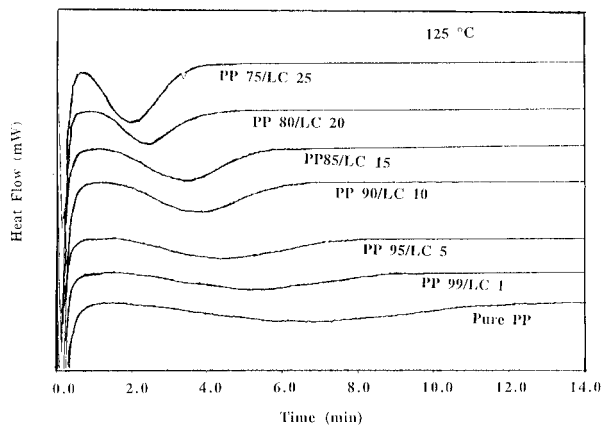

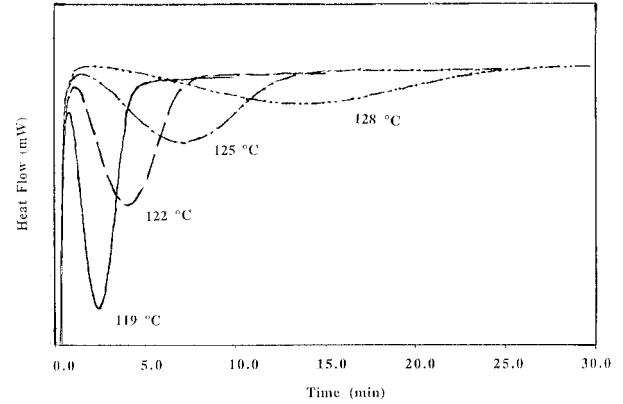**Figure 3** Isothermal crystallization of PP–LCP binary blends at 125°C.

Figure 4 DSC curves for pure PP crystallized at different temperatures.

$$1 - x = \exp(-kt^m) \tag{2}$$

where x is the reduced crystallinity (the fraction of total crystallinity after time $= t$), k is the crystallization rate coefficient, and m is the Avrami exponent. $t_{0.5}$, the time to attain 50% reduced crystallinity, is also a parameter obtained from the curves of x vs. time and the Avrami analysis. It is inversely related to crystallization rate.

Polarized hot-stage optical microscopy (HSOM) was performed using a Nikon Labophot 2 microscope and a Mettler FP82HT hot stage. Polymer specimens were cut using a microtome, and mounted on glass slides. The specimens were then heated to 200°C for 1 min then cooled to room temperature at 5°C/min. The HSOM was observed using a videocamera with digital image
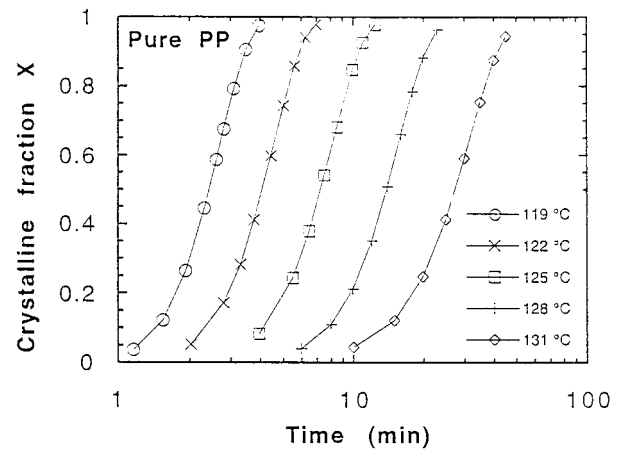

Figure 5 Plots of time vs. crystallinity of the pure PP at different temperatures.
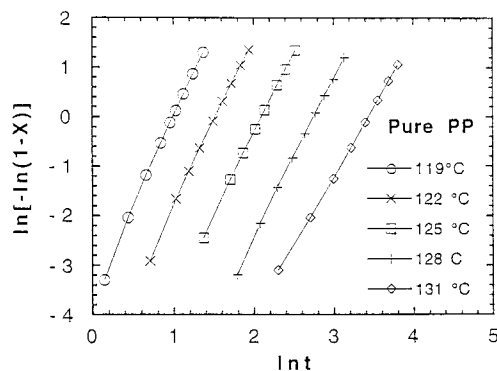
Figure 6 Plots of $\ln(-\ln(1-x))$ vs. $\ln(t)$ according to the Avrami equation.

capture, and the image was analyzed and enhanced using IPLab image analysis software. The HSOM images were used to study the morphology and nucleation.

RESULTS AND DISCUSSION

Figure 1 shows DSC cooling scans at 10°C/min for binary blends of LC3000 and PP. It can be seen that although the shape remains similar, the PP crystallizes at higher temperature with increasing LC3000 concentration. The peak positions and heat of fusion (shown as a function of the J/g of PP component) are shown in Table 1, where a change of 4°C in T_c between the homopolymer and the highest blend concentration is apparent. In addition, the total enthalpy liberated during crystallization is slightly greater for the blends. This can be understood in the following way. The liquid crystalline polyester crystallizes at a higher temperature than polypropylene (the PET phase of LC3000 crystallizing at approximately 145°C,[16] so just prior to the polypropylene crystallizing the system consists of solid particles of LCP in liquid PP. These solid particles are incompatible with polypropylene; however, they can act as nucleation sites, just as mineral or polar organic molecules provide nucleation. It appears that 5% (mass) of LC3000 is sufficient to saturate the blend with nuclei, and little change occurs at higher concentrations. Similar data is presented in Figure 2 for PP 80–LC 20 with varying amounts of added compatibilizer (PP-*g*-epoxy). As the compatibilizer is increased, the crystallization exotherm shifts to higher temperatures and the enthalpy of crystallization increases from 91.75 to 96.16 J/g. The compatibilizer is expected to decrease the particle size of the LCP phase, providing a larger interfacial area between PP and LCP. This will increase the nucleation activity of the LCP towards the PP.

A better understanding can be obtained by performing isothermal crystallization measurements at a range of temperatures as outlined above, an example of which is shown in Figure 3 for 125°C. The results can be compared with those for pure PP at several isothermal temperatures in Figure 4. The results from the isothermal data (Fig. 5) for the blends was then fitted to the Avrami equation [eq. (2), Fig. 6), and the results for the Avrami exponent (m) and the rate coefficient (as $\ln k$) are

Table II Avrami Exponent (m) and Rate Coefficient ($\ln k$) at Different Isothermal Crystallization Temperatures

| Temperature	119°C m	119°C $\ln k$	122°C m	122°C $\ln k$	125°C m	125°C $\ln k$	128°C m	128°C $\ln k$	131°C m	131°C $\ln k$	135°C m	135°C $\ln k$	138°C m	138°C $\ln k$
Pure PP	3.69	−3.71	3.61	−5.24	3.44	−6.91	3.42	−8.51	3.34	−9.54	3.31	−10.51	3.23	−11.83
PP 99/LC 1	3.72	−2.75	3.66	−4.44	3.62	−6.24	3.56	−7.91	3.52	−9.13	3.47	−9.98		
PP 95/LC 5	3.82	−2.60	3.76	−4.07	3.73	−6.32	3.66	−7.81	3.62	−9.01	3.54	−9.73	3.49	−11.12
PP 90/LC 10	3.77	−2.41	3.68	−3.88	3.66	−5.89	3.51	−7.51	3.52	−8.99	3.48	−9.71	3.37	−10.94
PP 85/LC 15	3.81	−2.12	3.78	−3.69	3.73	−5.45	3.62	−7.33	3.61	−8.49	3.56	−9.79	3.51	−10.81
PP 80/LC 20	3.79	−2.01	3.65	−3.65	3.64	−5.15	3.58	−7.12	3.52	−8.39	3.46	−9.39	3.38	−10.11
PP 75/LC 25	3.75	−1.81	3.69	−3.55	3.61	−5.11	3.52	−6.92	3.44	−8.20	3.41	−9.32	3.39	−9.89
PP80/LC20/C-1	3.88	−1.17	3.69	−2.83	3.64	−4.59	3.61	−6.20	3.53	−7.85	3.50	−8.23	3.41	−9.58
PP80/LC20/C-2	3.71	−1.18	3.70	−2.66	3.67	−3.85	3.60	−5.86	3.49	−7.82	3.42	−8.12	3.33	−9.47
PP80/LC20/C-5			3.77	−2.66	3.72	−4.22	3.59	−5.41	3.51	−7.49	2.35	−8.12	3.29	−9.24
PP80/LC20/C-10			3.72	−2.41	3.65	−3.91	3.61	−5.41	3.57	−6.73	3.31	−8.13	3.30	−9.01
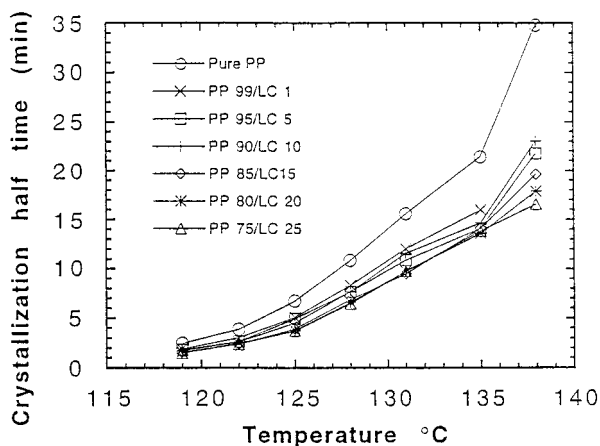
Figure 7 Effect of LCP on the PP crystallization half-time, $t_{1/2}$, in PP–LCP binary blends.

shown in Table 2. As expected, lower crystallization temperatures result in greater crystallization rates (less negative values of ln k) due to greater undercooling. It can also be seen (and supported by temperature scanning data from Fig. 1 and Table 1) that for a given crystallization temperature greater rates occur with the addition of LC3000, and this can be seen in the crystallization half-times, $t_{0.5}$, shown in Figures 7 and 8. Analysis also shows that the Avrami exponent increases slightly on average. The values range from 3.29 to 3.88, indicating that there is a combination of heterogeneous and homogeneous nucleation in the PP. The change in m is small, but increases on average as a function of addition of the LC3000 component. These results indicate the sensitivity of isothermal experiments to the effect of changes in concentration, as the results in Figure 1 could not differentiate blends with compositions greater than 10% (mass) LCP, although this is clear from the Avrami data. Clearly, the rate coefficient for crystallization increase (half-time decreases) with LC3000 content, and this can be attributed to more of the PP being adsorbed and nucleating on the LC3000 surfaces. When the grafted PP compatibilizer PP-g-GMA (Fig. 2) is added, the particle size of the liquid crystalline polyester decreased, thereby providing more surface for the same blend composition.

Crystallization occurred at a higher temperature, under constant cooling rate, when liquid crystalline polyester was present, again demonstrating the immobilization of polypropylene by

the dispersed particles. The effect was accentuated with compatibilizer. The crystallinity of polypropylene (ΔH) was increased slightly in the blends, and more so when the compatibilizer was present. This modification of PP is interfacial only since the two polymers are completely immiscible.

Figure 9 shows morphologies of four different specimens under the polarizing optical microscope. The morphologies of the pure PP. PP–LCP binary blends and PP–LCP-compatibilizer hybrids are significantly different. Figure 9(a) shows the spherulitic structure of the pure PP. The size of the PP spherulites is about 30 μm. Figure 9(b) shows the PP 95–LCP 5 binary blends. It was found that the LCP reduced the size of the PP spherulites. This is proposed to be due to PP being increasingly immobilized by adsorption onto the particle surfaces such that it can nucleate and crystallize at a higher temperature. This will produce smaller spherulites, because it will be equivalent to crystallization at a lower temperature; i.e., lower mobility of PP. Increased nucleation also helps formation of the smaller spherulites, because the Avrami m is increased slightly, while the rate was also increased. LCP particles can be identified among the PP spherulites. As the content of LCP increased to 20%, all of the image was occupied by LCP [see Fig. 9(c)]. Figure 9(d) is of the PP 80–LCP 20–g-epoxy 5 hybrid. It can be seen that a large number of small PP spherulites appeared. The LCP was able to strongly adsorb the grafted PP. The polarized optical microscopy confirms the conclusions from isothermal and cooling DSC. The spherulites of polypropylene are much smaller in the blends,
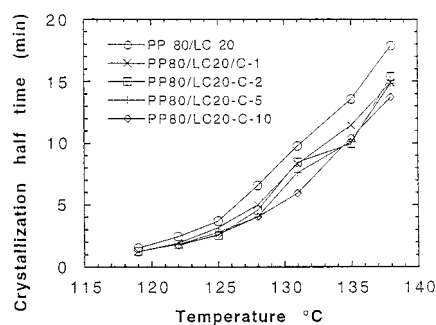

Figure 8 Effect of compatibilizer (PP-g-epoxy) on the crystallization half-time, $t_{1/2}$, in PP–LCP–PP-g-epoxy hybrids.
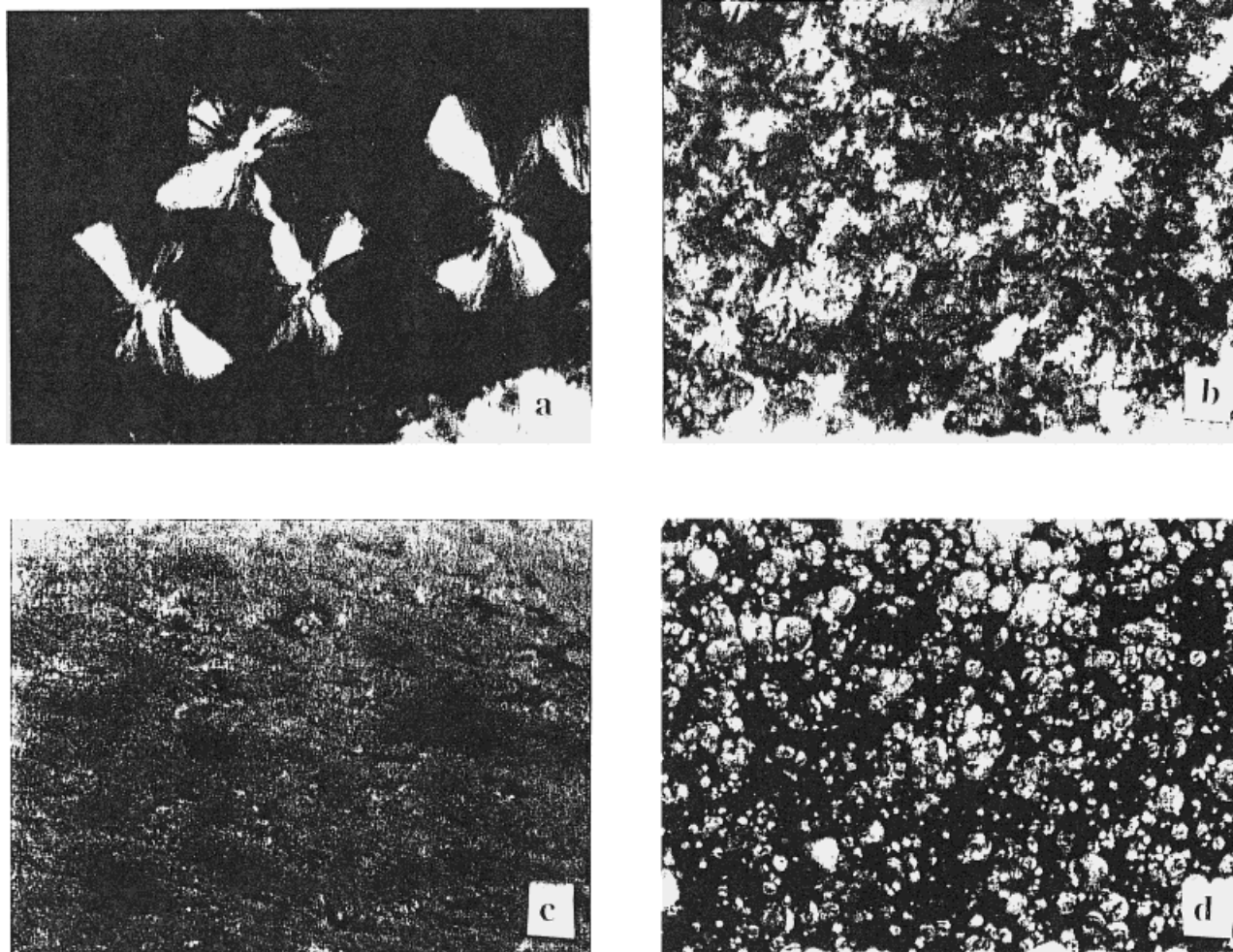
Figure 9 Morphologies of pure PP (a), PP 95–LCP 5 (b), PP 80–LCP 20 (c), PP 80–LCP 20–PP-*g*-epoxy 5 (d) under a polarizing microscope, ×160.

and smaller again when compatibilizer was present.

CONCLUSIONS

Liquid crystalline polyester was dispersed in polypropylene to provide a coarse two-phase incompatible blend. Glycidyl methacrylate grafted polypropylene was effective as a compatibilizer, and smaller particles of liquid crystalline polymer were formed with good interfacial adhesion. The crystallization of polypropylene was changed in the blend. The half-time decreased with liquid crystalline polyester content, and also decreased, at constant composi-

tion as compatibilizer was added. The spherulite size was decreased by the same order as the half-time. This is consistent with the liquid crystalline polyester acting as a nucleating agent for polypropylene.

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