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BLENDS OF LIQUID CRYSTALLINE POLYESTERS AND POLYETHYLENE TEREPHTHALATE - MORPHOLOGICAL STUDIES

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Abstract Polyethylene terephthalate (PET) was blended with two different kinds of liquid crystalline (LC) polyesters with the level of LC polyester varying from 5 to 15 weight %. Homogeneous samples were prepared by melt blending the polymers in twin screw extruder. The crystallization and morphology of these blends was studied with the help of differential scanning calorimetry(DSC), small angle light scattering (SALS), wide angle X-ray diffraction (WAXD), polarizing microscopy and scanning electron microscopy (SEM) techniques. DSC studies showed that the LC polyesters increase the rate of crystallization of PET in a manner similar to that of nucleating agents. WAXD showed that a significant level of crystalline orientation is produced in blends during extrusion under conditions which produce no orientation in PET. SEM studies on extruded strands show the presence of fibrous structures oriented along the extrusion direction. SALS and polarizing microscopy show the presence of anisotropic structures in melt quenched samples unlike the case of PET. The effect of LC polyesters on the crystallization and morphology of PET has been clearly demonstrated.

INTRODUCTION

Blending of two polymers can produce performance property parameters which sometimes can not be achieved by individual components.[1] The morphology and properties of a blend can be varied widely to suit specific application by changing its composition or its components. Several blend systems comprising of conventional thermoplastics have been developed in the past and new ones are being investigated showing

the continued interest in this area. Liquid crystalline(LC) polymers are the new additions to the family of polymeric materials hence the work on blends with a LC polymer as a component is just beginning to be reported.[2-7] Wilkes and coworkers[3,4] were the earliest to study the blends of a LC copolyester and polyethylene terephthalate (PET). They covered a large range of compositions with relatively high amount of LC polyester and showed significant effect of LC polyester on PET. Earlier work from our laboratory[8,9] showed that even low levels of LC polyester significantly affects the morphology and properties of PET thus it can be considered as a modifier for PET. In general the presence of LC polyester increased the rate of crystallization of PET and affected the crystal structure as well as the superstructure morphology. Melt spun fibers of blends showed orientation and had enhanced mechanical properties as compared to pure PET fibers[8]. In this earlier study only one kind of LC copolyester was used.

In the present study emphasis is given to investigate the morphology of PET blends with two different LC polyesters. The LC polyesters chosen were a) copolymer of 6-hydroxy-2-naphthoic acid & p-hydroxybenzoic acid (PHB), b) copolymer of PET and PHB in the molar ratio 20:80.

EXPERIMENTAL

Materials

Molding grade PET was obtained from Century Enka Plastics Company (India). LC copolyester of 6-hydroxy-2-naphthoic acid and PHB with the trade name Vectra A900 was obtained from Celanese Speciality Operations, New Jersey (USA) and will be hereafter referred as VLC. Copolyester of PET and

PHB containing molar ratio 20:80 was obtained from Tennessee Eastman Kodak Company (USA) and will be hereafter referred as KLC.

Sample Preparation

Two sets of blends were prepared, one with VLC designated as PET/VLC while the other with KLC designated as PET/KLC. The number at the end of each blend represents the amount of LC which was varied as 0,5,10 and 15 weight percent. Vacuum dried polymer granules of PET and the respective LC polymer were melt blended using Brabender Plasti-Corder equipment with twin-screw compounder (DSK 42/5) at 290°C. Extruded strands of the blends were quenched in cold water, granulated and the granules were dried before further processing. Compression molded films (approx. 100 μm thick) of PET, blends and LC polymers were prepared at 275°C under 3000 Lb/inch^2 pressure followed by immediate quenching in ice water mixture. Dried films were annealed at 140°C for two hours in a constant temperature silicone oil bath.

Thermal studies were carried out on a du Pont 1090 differential scanning calorimeter (DSC) using thin molded films. The samples were maintained at 350°C for two minutes in nitrogen atmosphere to destroy the anisotropy. Subsequently the samples were cooled at 20°C/minute upto 40°C and then again heated at 10°C/minute upto 350°C to obtain cooling and heating curves respectively.

Wide angle X-ray diffraction (WAXD) photographs were obtained for extruded rods while intensity vs. 2θ scans were recorded for compression molded quenched as well as annealed films using philips X-ray diffraction unit.

Morphological studies also involved the use of small angle light scattering (SALS), polarizing microscopy and

scanning electron microscopy (SEM). Thin molded films were examined by using a photographic SALS apparatus with 5 mw He-Ne source and a Lietz polarizing microscope. SEM studies were carried out on fractured surfaces of extruded rods and molded films using a Cambridge S4-10 Stereoscan SEM. All samples were fractured under liquid air. Extruded strands were fractured across as well as along the flow directions.

RESULTS AND DISCUSSION

Figure 1 shows cooling and heating curves for PET/VLC blends and the various parameters determined from these curves are given in Table I. From the cooling curves it can be

TABLE I Comparison of data from DSC thermograms of PET/VLC blend film samples.

Sample	T_m (°C)	ΔH_f (J/gm)	ΔH_c (J/gm)	T_c (°C)
PET	244.9	27.5	29.7	179.3
PET/VLC 5	251.2	32.1	36.4	198.1
PET/VLC 10	249.3	15.3	20.8	196.1
PET/VLC 15	251.6	15.9	21.3	197.4
PET/KLC 5	244.4	25.9	27.9	194.6
PET/KLC 10	236.9	27.8	19.0	179.1
PET/KLC 15	215.3	22.8	12.1	143.7

seen that temperature of crystallization (T_c) for the blends is appreciably higher as compared to that of PET. However, the difference between the blends with different VLC levels is not significant. These results suggest that VLC acts like a nucleating agent for the crystallization of PET and this effect probably reaches a maximum at a VLC level between 0 to 5 weight %. The heating curves of Figure 1

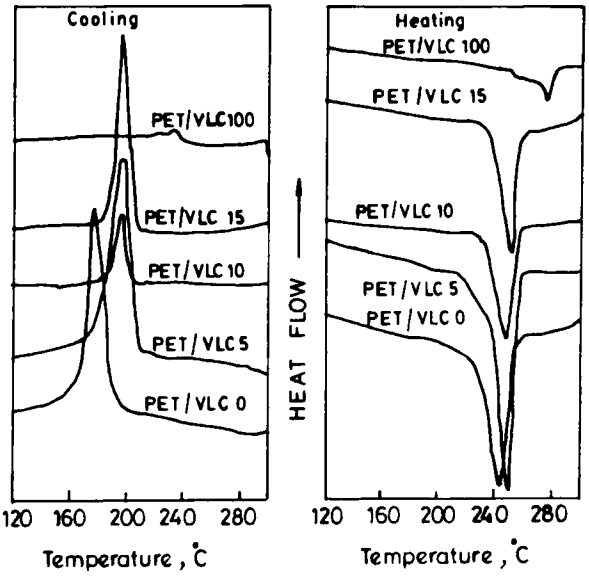


FIGURE 1. Cooling and heating DSC thermograms for PET/VLC blend films.

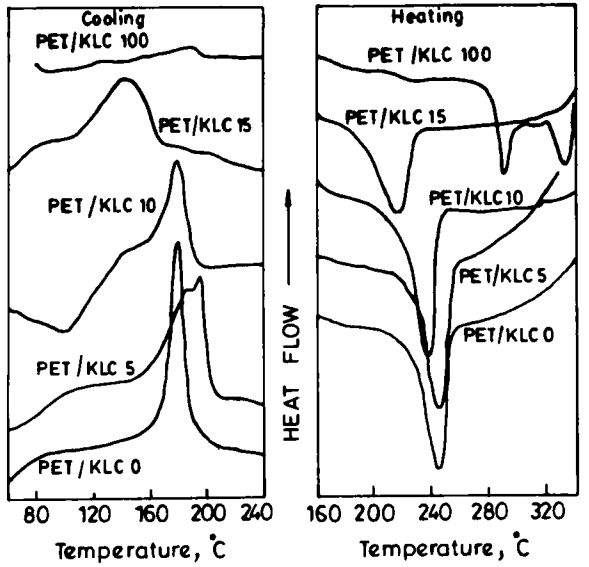


FIGURE 2. Cooling and heating DSC thermograms for PET/KLC blend films.

show that the melting temperature of the PET/VLC blends is slightly higher than that of PET. Heat of fusion as well as heat of crystallization first increased for the 5% VLC sample but then decreased for 10 and 15 weight % samples. This suggests that the crystals formed at higher VLC level are probably more imperfect due to an excessive nucleation effect thus showing a decrease in ΔH_c and ΔH_f values (Table I).

The cooling and heating thermograms for PET/KLC blends are given in Figure 2 and the values of parameters of these curves are given in Table I. Cooling curves show that T_c increases at 5 weight % KLC level but then decreases while the ΔH_c values decrease with the addition of KLC. Heating curves show a decrease in T_m as well as ΔH_f with the addition of KLC. These show that KLC acts as an effective nucleating agent only at very low levels. At higher levels KLC possibly destroys the symmetry of PET thus resulting in a decrease in order which is responsible for decrease in ΔH_f, ΔH_c and T_m values.

Photographic WAXD patterns from extruded strand of PET/VLC blends are shown in Figure 3. Pure PET shows a typical amorphous halo as expected while pure VLC shows a pattern representing a high degree of crystal orientation. The blend samples exhibit some crystalline orientation which tends to increase with VLC level. The background halo in the WAXD patterns of blends is probably because of amorphous PET in the system. WAXD intensity vs. 2θ scans of compression molded quenched films (Figure 4) show the presence of crystallinity in the PET/VLC and PET/KLC samples. Figure 5 shows WAXD intensity vs. 2θ scans for annealed samples. The d-spacing values from the diffraction peaks in these samples are given in Table II and clearly show

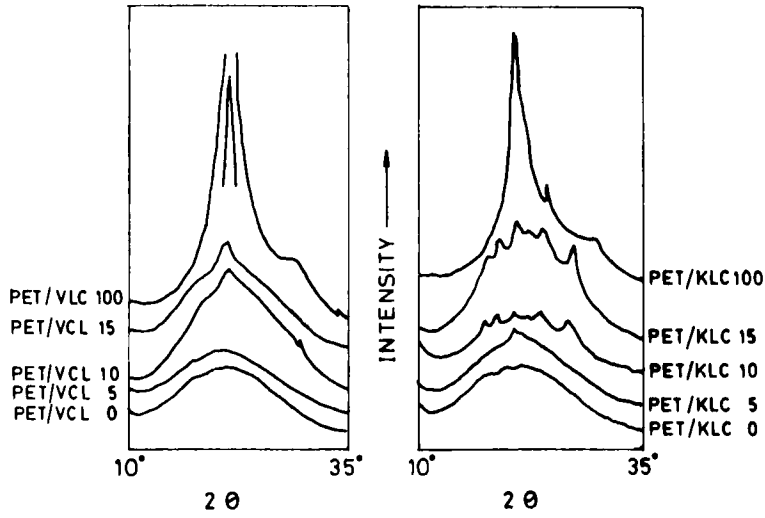


FIGURE 4. Wide angle X-ray diffraction intensity vs. 2θ plots for compression molded quenched PET/VLC and PET/KLC blend films.

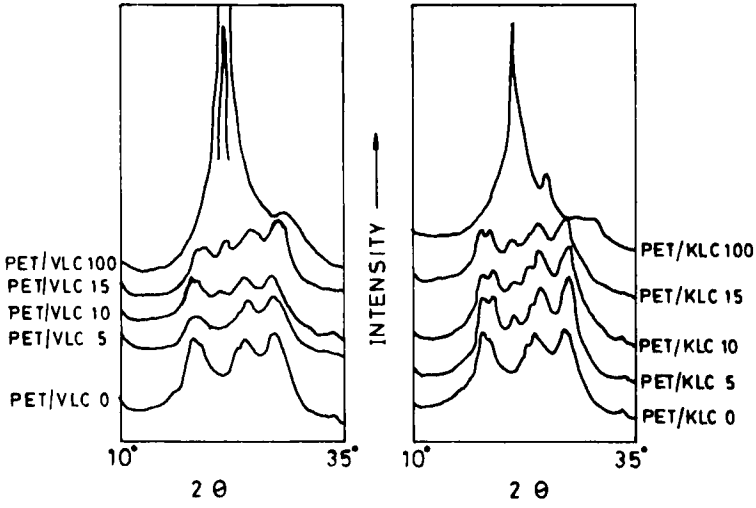
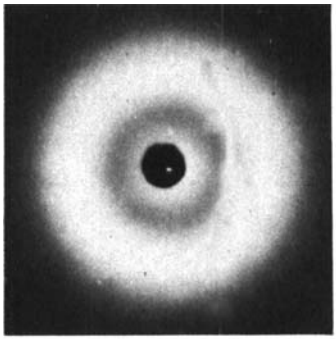
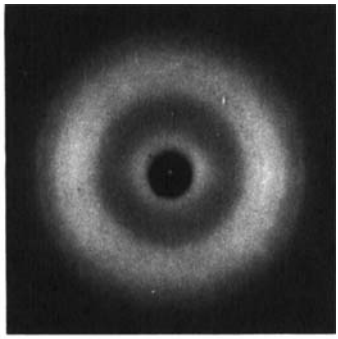


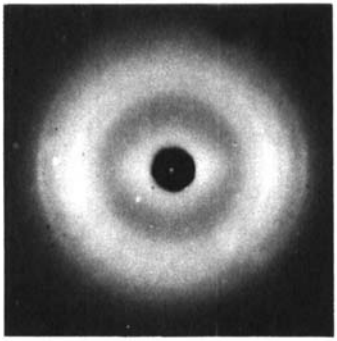
FIGURE 5. Wide angle X-ray diffraction intensity vs. 2θ plots for compression molded annealed PET/VLC and PET/KLC blend films.



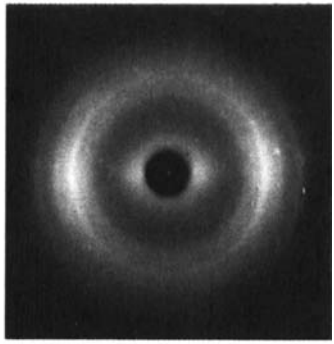
PET



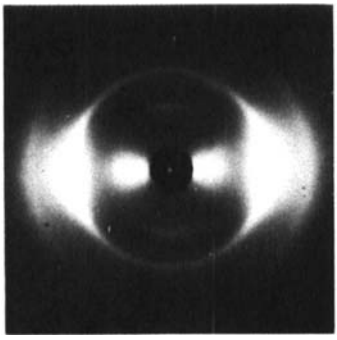
PET/VLC 5



PET/VLC 10



PET/VLC 15



PET/VLC 100

FIGURE 3. Wide angle X-ray diffraction patterns for extruded strands of PET/VLC blends.

TABLE II Comparison of d-spacing values (obtained from WAXD) for various diffraction planes for compression moulded annealed blend films.

Sample	d-spacing values (in Å) for planes		
	010	$\bar{1}10$	100
PET	4.82	3.65	3.24
PET/VLC 5	4.93	3.71	3.30
PET/VLC 10	5.10	3.77	3.33
PET/VLC 15	4.72	3.68	3.23
PET/VLC 100	4.15	-	3.12
PET/KLC 5	4.98	3.68	3.27
PET/KLC 10	4.98	3.71	3.27
PET/KLC 15	5.06	3.74	3.30
PET/KLC 100	4.25	3.59	3.00

that the crystal structure of PET may be affected due tp the presence of VLC. It was not possible to determine degree of crystallinity for the blends since corresponding amorphous samples could not be prepared. Blends based on KLC show similar results by WAXD and the d-spacing variation with KLC level is given in Table II.

Figure 6 shows H_v SALS patterns for PET/VLC and PET/KLC blend films quenched from the melt. These patterns show the presence of anisotropic superstructures probably due to the LC component since under similar conditions pure PET does not show any superstructure. The patterns of Figure 6 have a high intensity in the center and thus obscure the real angular dependence. However, a close examination reveals these patterns to be typical for scattering by rod-like superstructures. The V_v patterns were circular and showed a significantly higher intensity than the corresponding H_v patterns. This suggests a high level of density fluctuation due to the non-volume filling nature of the

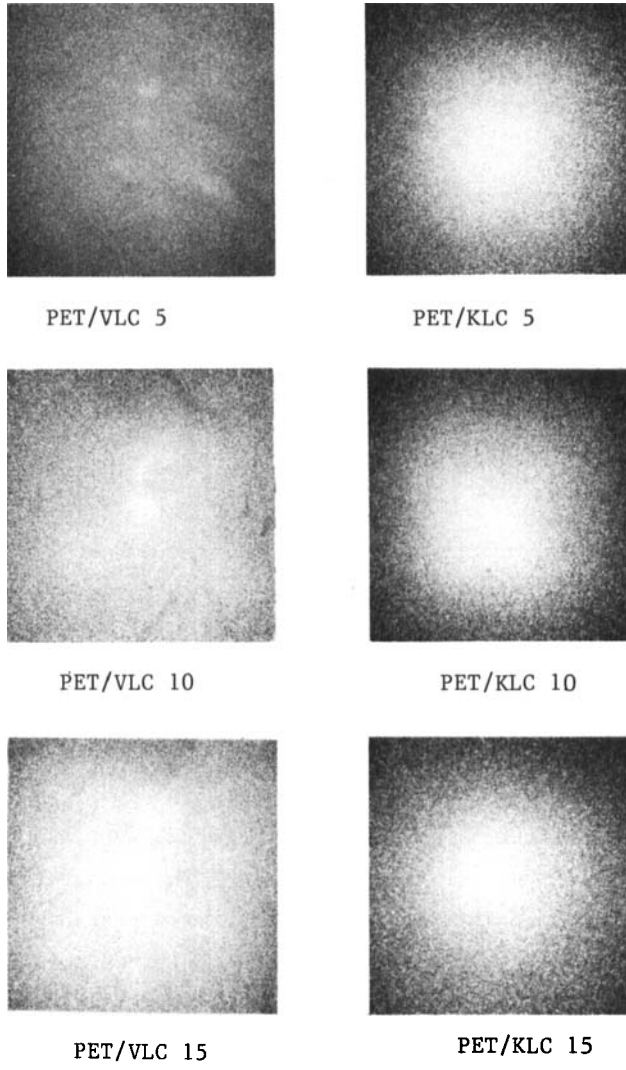


FIGURE 6. H_v SALS patterns for quenched PET/VLC and PET/KLC blend films.

scattering system. The SALS photographs are in general agreement with the theoretically predicted patterns from LC polymers on the basis of orientation fluctuations[10] arising from anisotropic domains or disclinations.

Figure 7 shows polarizing microscopy photographs for PET/VLC and PET/KLC blend films quenched from the melt. These micrographs support the presence of anisotropic entities which are typical of LC polymers. Furthermore, these are non-volume filling thus supporting the density fluctuations which resulted in higher V_v intensity in SALS.

Scanning electron micrographs of the cross-section of fractured extruded strands for PET, VLC and KLC as well as the PET/VLC and PET/KLC blends are shown in Figure 8. Both VLC and KLC exhibit the presence of oriented structures, with VLC showing a more fibrous structure while PET shows no structure or orientation. All the blend samples clearly show the presence of oriented rod shaped structures which obviously have been pulled out during fracture. The pores in the micrographs represent the holes left by the rod like entities pulled out on the other corresponding fractured surface. These are believed to be formed from the LC component in the blend during the extrusion process in which the LC domains get oriented in the flow direction. The number of such oriented strands increases with an increase in the level of LC polymer from 5 to 15 wt. %. The rod-like structures have a diameter of about 7 microns for PET/VLC 15 blend and a diameter of about 6 microns for PET/KLC 15 blend. Their appearance in fractured cross-section is similar to that of short glass fibers in reinforced thermoplastics. These structures can also be considered as reinforcing entities for the base polymer PET. Fractured cross-sections of annealed extruded strands show SEM

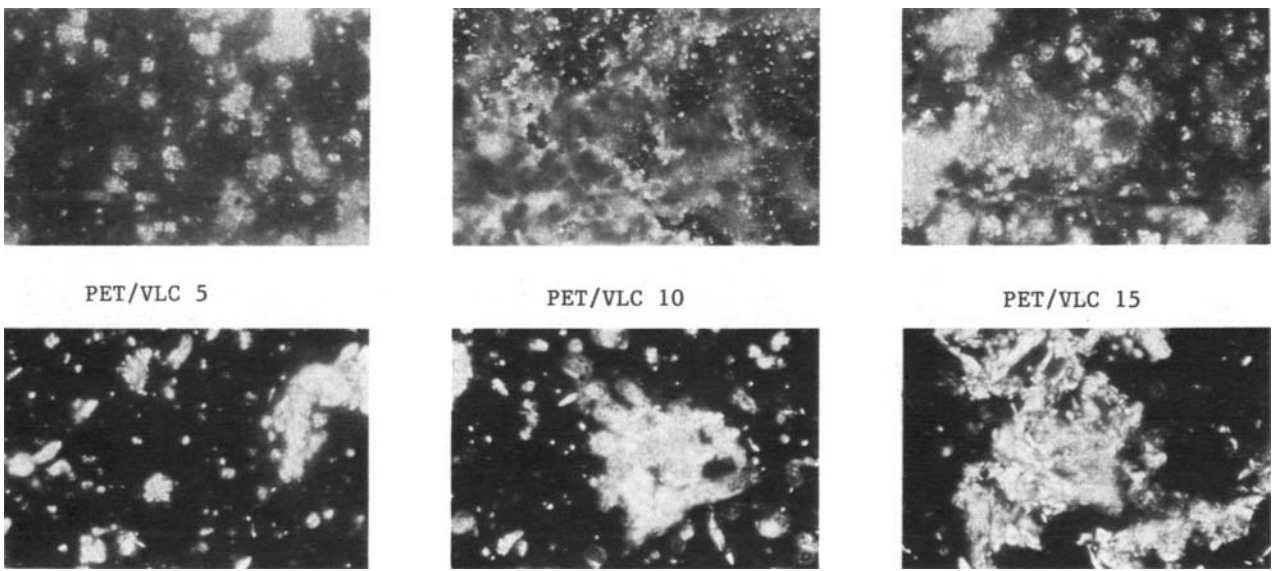


FIGURE 7. Polarizing micrographs for quenched PET/VLC and PET/KLC blend films.

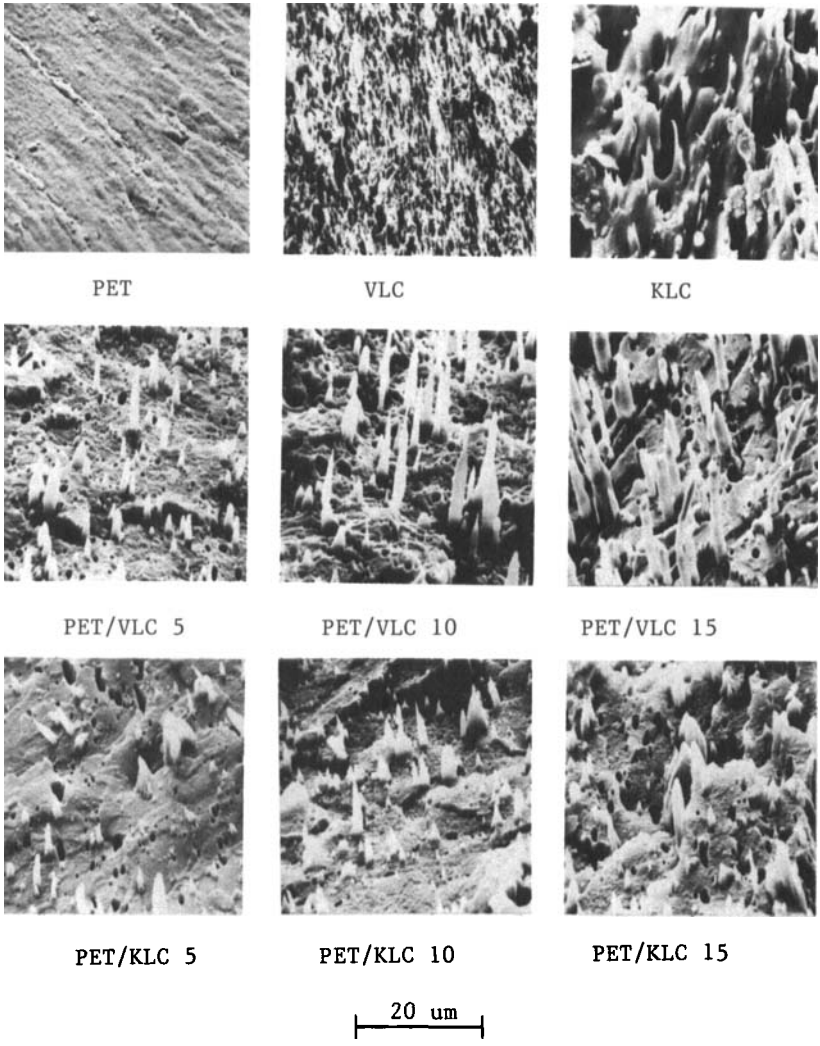


FIGURE 8. Scanning electron micrographs of fractured cross-section of extruded strands for PET, VLC, KLC and PET/VLC and PET/KLC blends.

photographs similar to those of unannealed samples described above and hence are not presented here. This shows that the annealing process does not affect the LC structures but affects only the crystallization of PET as was earlier observed by WAXD.

SEM studies of the fractured surface along the flow direction of the strands were carried out by splitting the strand lengthwise and their micrographs are presented in Figure 9. As before PET does not show any unusual structures while VLC and KLC clearly show the presence of fibrous structures with a preferred orientation in the flow direction. The blend samples clearly show the presence of long fibers imbedded in the background matrix. In the case of VLC blends these structures are much longer fibrous structures which appear to be almost continuous in the matrix. On the other hand, the KLC blends show the presence of relatively short and not totally continuous fiber like structures. The diameter of these fibrous structures increases with an increase in the amount of LC component. These observations are supportive of the fibers seen in the fractured cross-section. They also explain the crystalline orientation observed by WAXD studies as mentioned earlier.

SEM micrographs of fractured cross-section from compression molded films of PET, VLC, KLC as well as PET/VLC and PET/KLC blends are shown in Figure 10. Pure VLC and KLC polymers show randomly oriented fibrous structure while PET shows homogeneous non-fibrous structure. In the PET/VLC blends, VLC appears only in spherical shaped entities while in PET/KLC blends, KLC is dispersed in small rod like shape as well as elliptical shaped entities. The size of LC polymer spheres/rods increases with increase in LC polymer from 5% to 15% in the blend. In all cases the

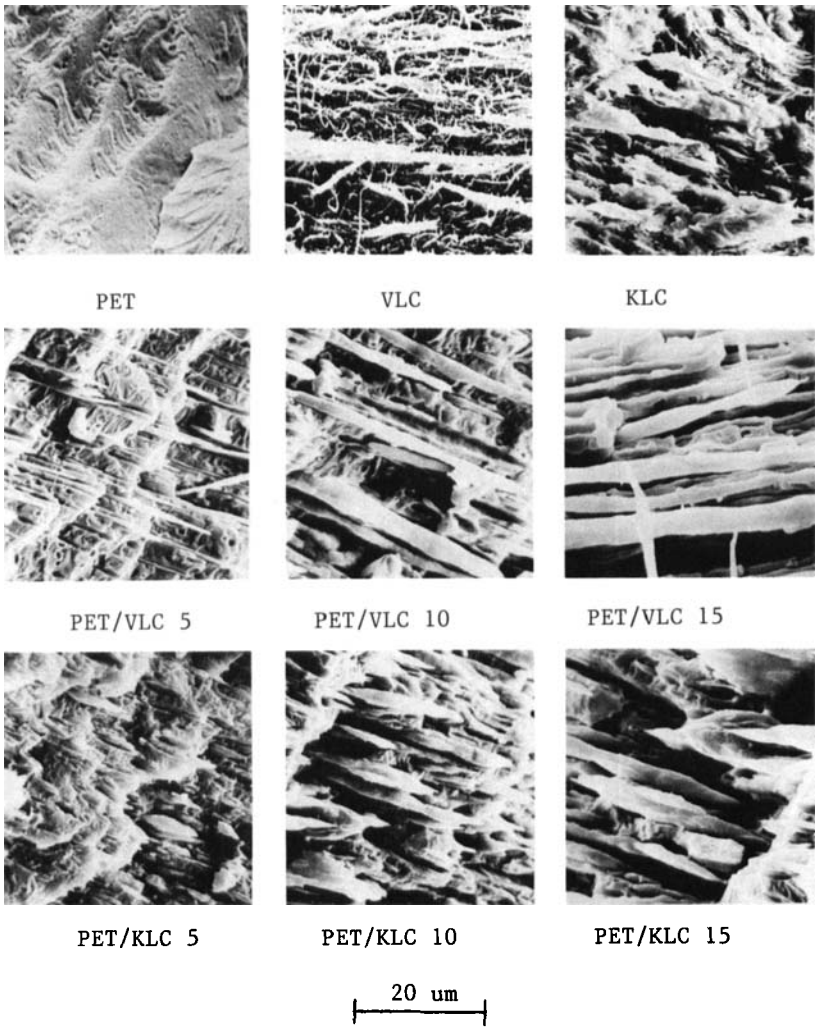


FIGURE 9. Scanning electron micrographs of fractured surface of extruded strands along the flow direction for PET, VLC, KLC and PET/VLC and PET/KLC blends.

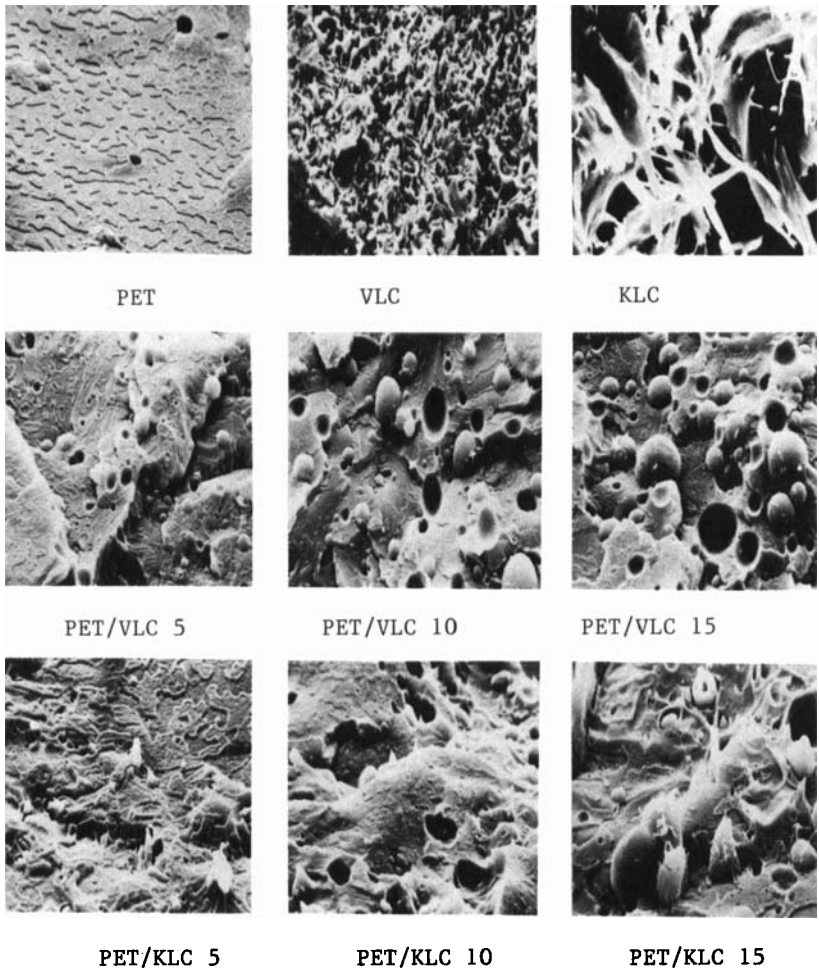


FIGURE 10. Scanning electron micrographs of fractured cross-section of compression molded films for PET, VLC, KLC and PET/VLC and PET/KLC blends.

LC polymers appear to be very well dispersed in the PET matrix showing that the mixing of the two components is good.

CONCLUSIONS

In this study we have successfully prepared some blends of PET as the major component and LC polyesters as the minor component. Some of the salient observations of this study are :

1. The LC polymers appear to nucleate and hence accelerate crystallization rate of PET as seen by DSC and WAXD results. This is in support of our earlier work[8,9]
2. Extrusion of the blends results in significant crystalline orientation as seen by WAXD which is attributed to the alignment of the LC component in the flow direction.
3. SEM studies of extruded blend strands reveal the presence of fiber-like structures arising from the orientation of the LC component. This fiber-like phase can be seen as a reinforcing phase for the matrix polymer.
4. SALS and polarizing microscopy show the presence of anisotropic entities in melt quenched films probably from the LC domains.

It has been clearly shown that the addioion of a liquid crystalline polymer to a semicrystalline polymer significantly modifies the crystallization behavior and morphology of the latter. This can be used to advantage in order to enhance the performance properties of semicrystalline polymer specially those used as synthetic fibers or engineering plastics.

REFERENCES

1. D.R. Paul and S. Newman Ed., Polymer Blends, Academic Press, New York (1978).
2. M. Koyanagi, M. Kajiyama, F. Kumamaru and T. Ohno, Polym. Prep. Am. Chem. Soc., Div. Polym. Chem., 24, 211 (1983).
3. E.G. Joseph, G.L. Wilkes and D.G. Baird, Polym. Prep., Am. Chem. Soc., Div. Polym. Chem. 24, 304 (1983).
4. E.G. Joseph, G.L . Wilkes, and D.G. Baird, Polymeric Liquid Crystals, A. Blumstein Ed., Plunum Press, New York (1985).
5. A. Siegmann, A. Dagan and S. Kenig, Polymer, 26, 1325 (1985).
6. K.G. Blizard and D.G. Baird, Polym. Sci. and Engg., 27, 653 (1987).
7. R.A. Weiss, W. Huh and L. Nicolais, Polym. Sci. and Engg., 27, 684 (1987).
8. S.K. Bhattacharya,Ph.D. Thesis, Studies on the Characterization of Liquid Crystalline Polyesters, IIT Delhi, India (1986).
9. S.K. Bhattacharya, A. Tendolkar and A. Misra, Molecular Crystals & Liquid Crystals, (to appear)
10. R.S. Stein and S. Rojstaczer, Polym. Prep., Am. Chem. Soc., Div. Polym. Chem., (to appear)