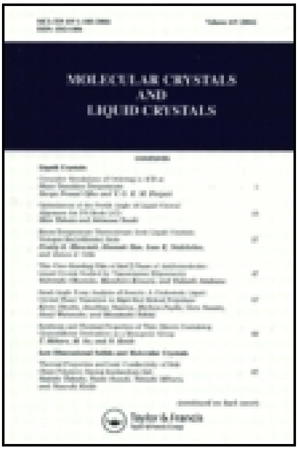

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Blends of a Liquid Crystalline Polyester with Polyethylene Terephthalate

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BLENDS OF A LIQUID CRYSTALLINE POLYESTER WITH POLYETHYLENE TEREPHTHALATE

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Abstract Morphology of blends of Liquid Crystalline (LC) co-polyesters and polyethylene terephthalate (PET) with a varying percentage of the liquid crystalline component were studied primarily by small angle light scattering (SALS), polarising microscopy and wide angle X-ray diffraction. The crystallization behaviour of these blends was studied with the help of density measurements and differential scanning calorimetry (DSC). It was observed that a small amount of LC component in PET changes the morphological and crystallization behaviour of PET. It also affects the mechanical properties of PET significantly.

INTRODUCTION

Studies on the blends of liquid crystalline (LC) copolyesters with PET have been reported by Wilkes and Coworkers[1-2]. Nucleation of PET by the LC copolyester as well as various other significant changes in morphology and rheology were observed by them. However, the amount of LC polyester blended with PET was rather large (30, 50 & 70 wt. %). At such high concentrations of the LC component it is not really a modifier for PET but gets diluted by the presence of PET. LC polymers have also been blended with other amorphous as well as crystalline polymers to give interesting properties[3,4]. The main aim of this study is to modify the properties of PET by the addition of relatively small amounts of a LC polymer.
The LC Polymer choosen was a copolyester of PET and

p-hydroxybenzoic acid (PHB) in a 60:40 mole ratio. Since the copolyester has PET as one of its components, it is expected to form a compatible blend with PET.[1]

EXPERIMENTAL

The LC polyester was obtained in the form of flakes from Eastman Kodak Company, USA and henceforth it will be referred as KLC. The PET used was obtained from century Enka Plastics, India. Samples with a varying KLC levels prepared were as follows: PET/KLC0, PET/KLC3, PET/KLC5, PET/KLC8, PET/KLC10, PET/KLC16, PET/KLC20, PET/KLC50, PET/KLC100. The number denotes the amount of KLC in the blend in terms of weight percent. PET and KLC samples identified as PET/KLC0, PET/KLC100 were used as controls.

The two components were blended in a melt screw extruder (Brabender Plasticorder) at 280°C. For thermal studies duPont 1090 thermal analyser was used with a heating rate of 10°C/min and a temperature scan range from 50°C to 350°C. X-ray diffraction studies were carried out on a Philips X-ray diffraction unit. For small angle light scattering (SALS) studies a 5mW Melles Griot He-Ne Laser source was used[5]. For temperature variation in SALS as well as polarizing microscopy studies, a Mettler hot stage with FP-80 program controller was used with temperature scan range from 50° to 300°C at heating and cooling rates of 10°C/min. The density measurements were done with the help of a density gradient column prepared from carbon tetrachloride and xylene. The samples for the density measurements were isothermally crystallized from the melt at 100°C.

RESULTS AND DISCUSSION

Figure 1 shows some representative DSC thermograms of the melt blended granules. The melting temperature of the

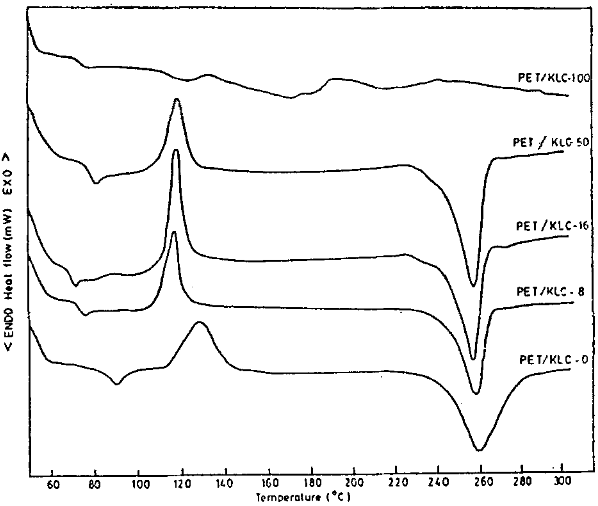


Figure 1. DSC thermograms for PET/KLC blend samples; heating rate = 10^{o}C/min

Table I: Tabulation of data from DSC thermograms of PET/KLC blend film samples

Sample	Tg(^{o}C)	Tc(^{o}C)	Tm(^{o}C)	ΔH_f (cal/gm)	ΔH_c (cal/gm)
PET/KLC0	-	129.9	258.3	9.77	4.25
PET/KLC8	75.5	116.3	257.4	16.80	8.63
PET/KLC16	71.3	118.1	256.2	14.48	7.67
PET/KLC50	80.4	118.1	257.0	11.71	4.80
PET/KLC100	-	-	-	-	-

blends was about the same as that of pure PET. Heat of fusion of the blends was slightly lower than that of PET but there is no definite correlation with KLC level. The DSC thermograms of the compression moulded films and subsequently quenched films showed that in general the T_g, cold crystallization temperature (T_c) and width of crystallization exotherm decrease with increase in the KLC content of the blends. The heat of fusion and crystallization increase substantially from PET/KLC0 to PET/KLC8 but then decrease steadily with further increase in the KLC content of the blends (Table I). The heat of fusion values for PET/KLC8,PET/KLC16 film samples (16.8 and 14.5 Cal/gm) correspond to 56% and 48% crystallinity respectively which are rather high values. It is thus believed that a large amount of localized orientation exists in the system. Another interesting observation is that the DSC scans for both the granule and film samples of the blends were much smoother than the DSC of pure KLC even at high levels of KLC. This suggested that KLC crystallizes in a much more orderly fashion in the presence of PET. In fact, it may be co-crystallizing with PET.

Figure 2 shows H_v SALS patterns for PET/KLC16 films as a function of temperature. Figure 3 shows the H_v SALS patterns for PET/KLC0, PET/KLC8 and PET/KLC50, one below T_m of PET and the other above it. For the pure KLC film sample a circular H_v scattering pattern was observed which could not be attributed to a distinct superstructure. This may be due to multiple scattering. On the other hand, for crystallized blend samples, 4 lobe cloverleaf type H_v scattering patterns with lobes at 45° to the polar direction were observed. They also showed a maximum in scattering intensity as is typical of PET spherulites. The very small

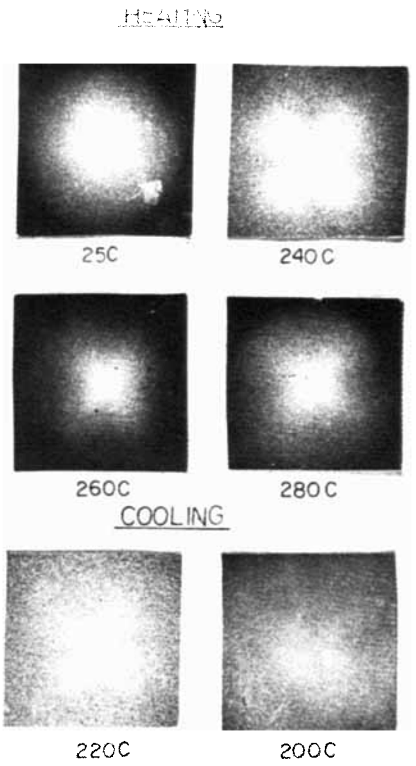


Figure 2. H_v SALS patterns for PET/KLC16 sample during heating & cooling.

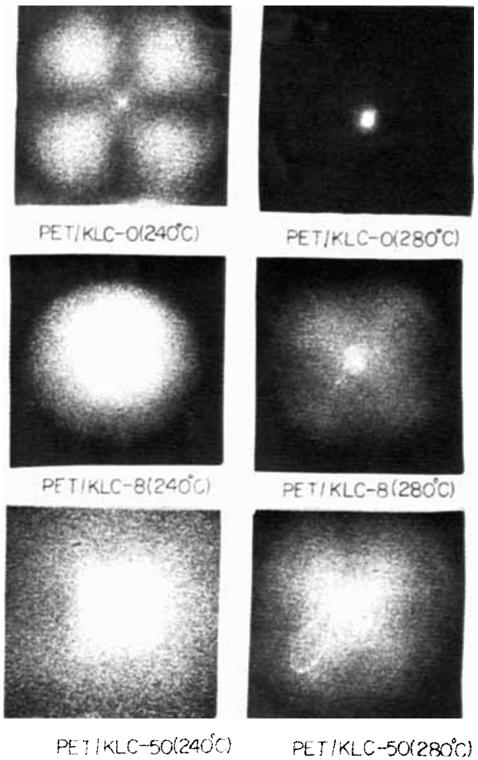
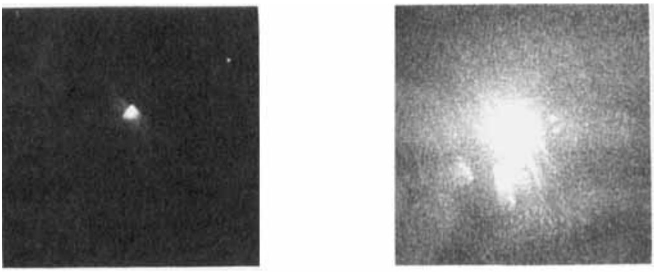


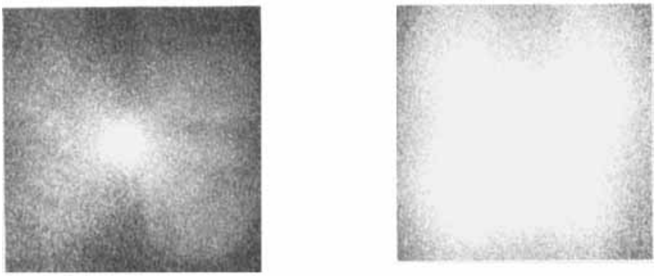
Figure 3. H_V SALS patterns of PET/KLC blend samples.

scattering pattern for the blend samples indicate large spherulites. When the blend films were heated to the T_m of PET, the spherulitic pattern disappeared and scattering intensity was found to drop significantly. At that temperature a very big rod-like pattern appeared with very low scattering intensity. The rod-like pattern persisted up to 300°C, the maximum temperature of this study. This is in agreement with the theoretically predicted patterns from LC polymers on the basis of orientation fluctuations[6] arising from anisotropic domains or disclinations. Pure PET, however, did not show any scattering beyond its T_m (Figure 3). Furthermore, cooling the blend samples from 300°C, the rod-like pattern stayed up to 220°C and spherulitic pattern appeared just below 220°C, the temperature at which crystallization of PET begins. The spherulites subsequently grew and the pattern started becoming smaller as seen in Figure 2 for PET/KLC16. Blend samples PET/KLC3, PET/KLC5, PET/KLC10, PET/KLC20 also show similar behaviour. Rod-like H_V scattering patterns from some of the samples are shown in Figure 4. Corresponding V_V scattering patterns for the blends showed a very high intensity compared to that of the H_V patterns suggesting that the nematic phase is present only in small quantity. The appearance of rod-like pattern after the melting of PET is probably due to the scattering from nematic domain of liquid crystalline polymer in the liquid state.

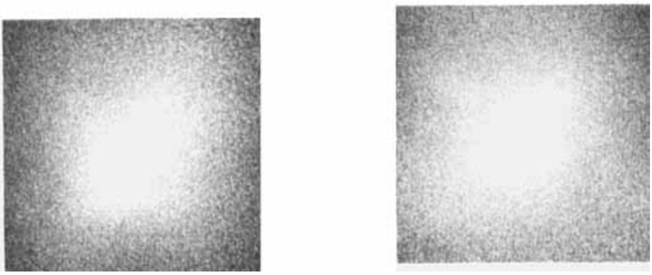
The presence of liquid crystalline domains when PET has completely melted supports the idea of nucleation of PET by KLC. However, the size of the spherulites in blends was found to be greater than that in PET which is in contradiction since the nucleation phenomenon should have decreased the average spherulitic radius. This observation



a) PET/KLC0 b) PET/KLC3



c) PET/KLC5 d) PET/KLC10



e) PET/KLC16 f) PET/KLC20

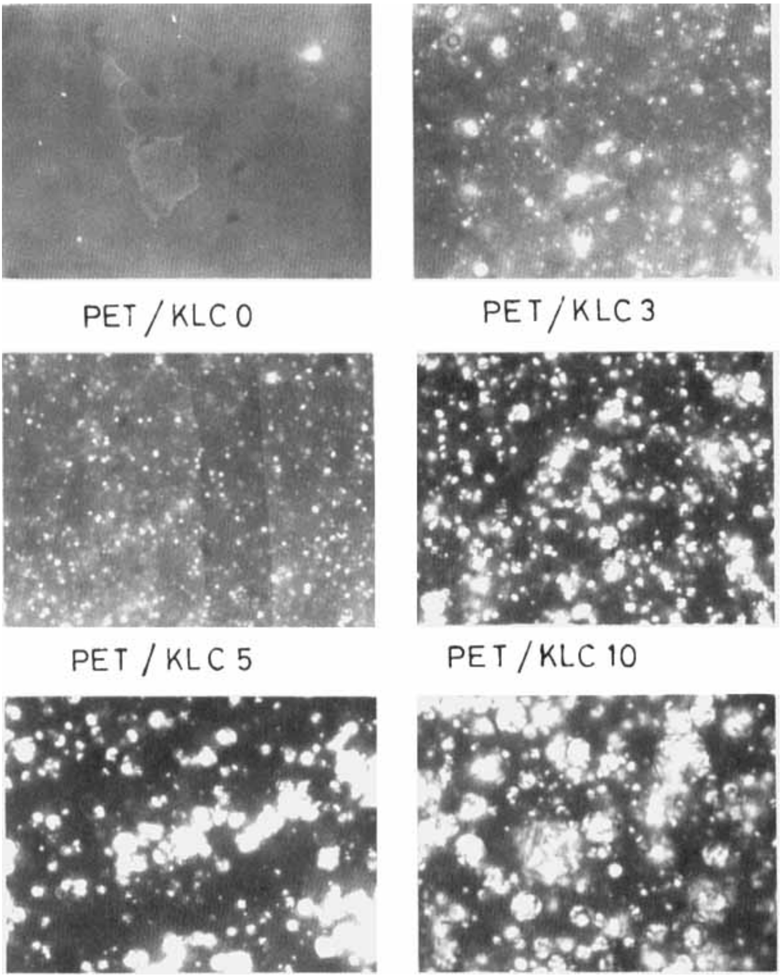
Figure 4. H_v SALS patterns for PET/KLC blend samples quenched from the melt.

coupled with DSC observations suggest that KLC not only acts as a nucleating agent for PET crystallization but also takes part in subsequent growth of structures.

Figure 5 shows that the polarizing micrographs of PET/KLC0, PET/KLC3, PET/KLC5, PET/KLC10, PET/KLC16 and PET/KLC20 quenched from the melt. PET/KLC0 does not show any depolarized light intensity suggesting that the PET melt is completely isotropic, but as the amount of KLC in the blend goes on increasing the intensity of the depolarized light also increases. The photomicrographs clearly show the presence of LC domains in the PET matrix which provide anisotropic fluctuations. The photomicrographs of the crystallized blend samples also show the presence of LC structures but are not presented here.

Figure 6 shows plots of reduced crystallinity versus time obtained from density measurements for blend samples isothermally crystallized from the melt at a temperature of 110°C. The curves are sigmoidal in nature from which the half time of crystallization values are obtained and plotted as a function of KLC level in Figure 7. It can be clearly seen that the rate of crystallization of PET is significantly enhanced by the presence of KLC thus demonstrating the nucleation effect of the LC component.

Figure 8 presents wide angle X-ray diffraction patterns for some melt spun blend and pure component fibre samples. Figure 9 gives the intensity versus diffraction angle plots. PET fibres show only amorphous scattering with no orientation while the blend fibres show significant amorphous scattering along with orientation. The presence of some amount of crystallinity is also indicated. Preliminary analysis showed the d-spacing values in the blend samples to be a bit lower than those of PET suggesting that



PET / KLC 0

PET / KLC 3

PET / KLC 5

PET / KLC 10

PET / KLC 15

PET / KLC 20

Figure 5. Polarizing photomicrographs for PET/KLC blend samples quenched from the melt.

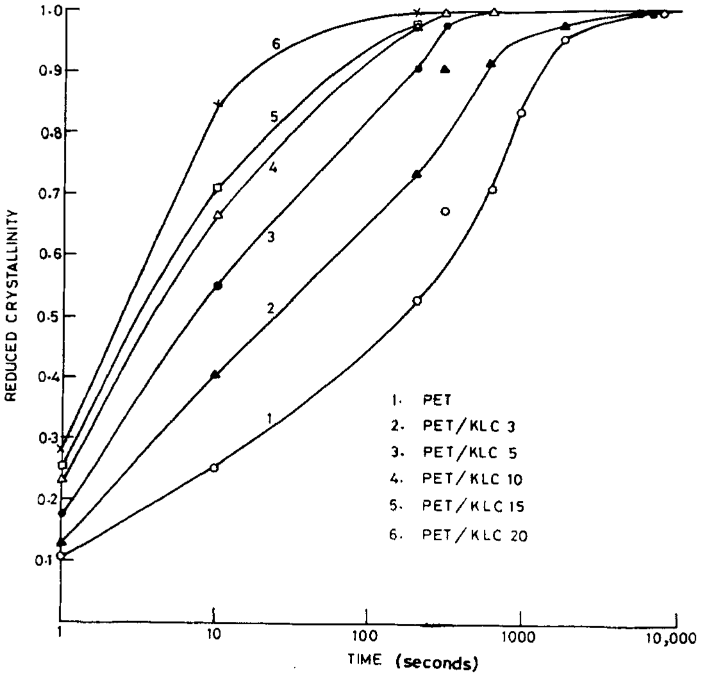


Figure 6. Plots of reduced crystallinity of PET/KLC blends, (T_c=110°C)

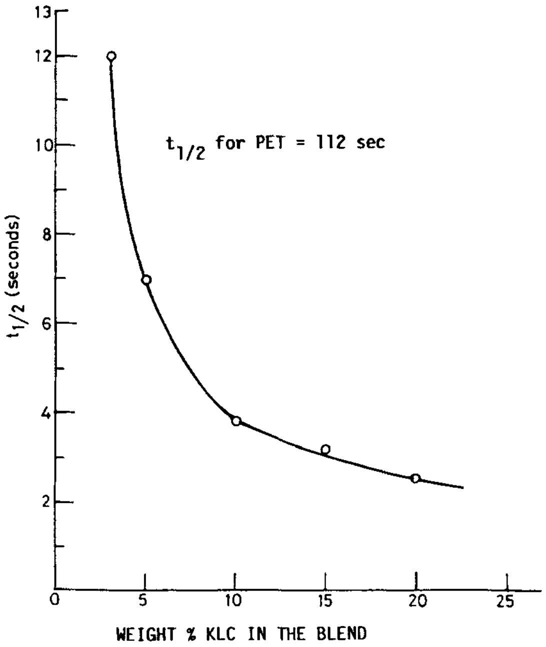
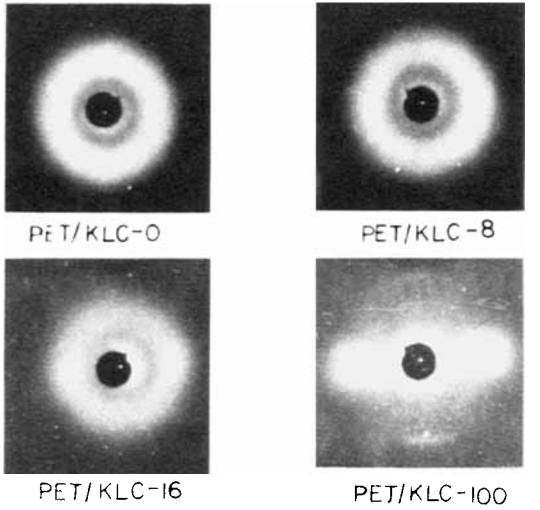


Figure 7. Half time of crystallization as a function of KLC in the blend, (T_c=110°C)



PET/KLC-0 PET/KLC-8

PET/KLC-16 PET/KLC-100

Figure 8. Wide angle X-ray diffraction patterns from melt spun fibres of PET/KLC blends.

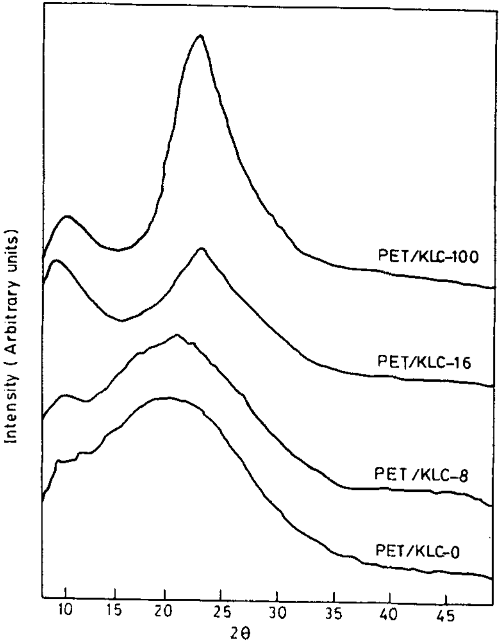


Figure 9. Wide angle X-ray diffraction intensity plots of PET/KLC blends.

KLC co-crystallizes with PET to produce a slightly different crystal structure. These observations suggest that KLC affects the orientation of chains during melt spinning thus resulting in fibres which have significant orientation & crystallinity unlike the case of pure PET which gives amorphous unoriented fibres.

Table II lists the mechanical properties of melt spun fibres of the blends and pure components as well as spun and drawn PET fibres. Spinning of PET/KLC50 blend resulted in very brittle fibres and thus were not tested. The results show that the initial modulus and tenacity of the melt spun fibres increases with increase in KLC content in the blends while elongation decreases. The mode of failure also changes from brittle to ductile at higher KLC levels. These results show that the presence of a LC component has a significant effect on the mechanical properties of PET which can be used to advantage.

Table II: Mechanical properties of PET/KLC blend fibres

Sample		Type of failure	Initial modulus (gms/tex)	Tenacity gm/tex	Elongation (%)
PET/KLC0	As-spun	Ductile	1.14	0.036	326.5
	DR=1.5	"	1.67	0.133	260.0
	DR=2.25	"	2.78	0.160	174.0
	DR=3.0	"	5.10	0.180	96.0
PET/KLC8	As-spun	Ductile	3.65	0.032	34.7
PET/KLC16	As-spun	Brittle	5.88	0.047	2.2
PET/KLC100	As-spun	Brittle	12.96	0.292	2.0

CONCLUSIONS

a) Thermal and mechanical studies indicate that the blends are homogeneous in nature.

b) SALS studies reveal the presence of ordered domains after the melting of PET due to the LC polymer. These ordered domains are probably responsible for nucleating the crystallization of PET.

c) Polarizing microscopy clearly shows the presence of LC domains both in quenched and crystallized samples.

d) Crystallization rate of the blends were significantly higher than that of PET suggesting that KLC acts as a nucleating agent for PET.

e) X-ray diffraction shows that the presence of KLC results in significant orientation and crystallinity during melt spinning probably due to the orientation of LC domains and their nucleating effect.

f) The melt spun fibres show high modulus and tenacity due to higher crystallinity & orientation.

g) The blending of KLC in PET results in several desirable properties which can be advantageously used for several practical applications.

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