Structure -Properties Relations of Polypropylene/ Liquid Crystalline Polymer Blends

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Abstract: The blends of polypropylene (PP) with glass filled thermotropic liquid crystalline polymer (LCP-g) have been prepared by melt mixing techniques at different blend ratios. The thermal, dynamic mechanical, crystalline and morphological characteristics of these blends were investigated. Higher percent crystallinity was observed for 10% level of LCP-g in the blend in comparison to that of other blend ratios. The thermal stability increased with LCP-g concentration in the blend with PP. The variation of storage modulus, stiffness and loss modulus as a function of blend ratios suggested the phase inversion at the 50% level of LCP-g in the blend. The scanning electron microscopy (SEM) photographs showed the creation of voids and destruction of the fiber structures during the dynamic mechanical measurements. Processing behavior of the blends depended on the fiber forming characteristics of LCP-g, which again varied with the molding temperatures.

Keywords: polypropylene, liquid crystalline polymer, dynamic mechanical properties, thermal properties, morphology, rheology.

Introduction

The characteristics of polymer blends depend on the amount and the properties of the individual polymers as well as on the mode of dispersion, the size and shape of the dispersed material and the interaction between the phases.[1] More recently, the blending of conventional thermoplastics with liquid crystalline polymers (LCPs) has attracted considerable scientific and industrial interest. LCPs generally possess rigid-rod like molecular chains and can exist in oriented polydomains.[2] The rigid rods oriented along the flow field lines should produce a lower resistance of LCPs to flow than unordered macromolecules. The majority of studies are confined to the relationship between morphology, rheology and mechanical properties of LCP blends.[3-7] Most of the blends of LCP with a thermoplastic are immiscible.[8-12] The problem of interfacial interaction enhancement becomes extremely important in immiscible blends. In self-reinforced composites, fibers can easily transfer mechanical load, even in the absence of good adhesion at the interface between the LCP fibers and the matrix. It was also obvious that properties of these self-reinforced composites can be further enhanced by an improvement of interfacial interaction. So, the interfacial interaction between components is an important factor to obtain a product with good mechanical properties. This can be realized by the proper choice of the components for blending with LCP.

Current literatures revealed that there are limited numbers of works of LCPs with polypropylene (PP). Bualek-Limcharoen *et al.*[13] studied the effect of compatiblizer on mechanical properties and morphology of LCP/PP blends. Seppala *et al.*[14] reported the injection molded blends of LCP with PP. According to them, LCP was acting as a reinforcing agent in the polymer matrix to improve their dimensional and thermal stability. Morphology of PP/LCP blends was also found to be affected by the use of different mixing equipment.[15] In this work, we have studied the blends of PP and glass fiber filled LCP (LCP-g). The dynamic, thermal, microstructure, morphological and rheological characteristics of these blends were investigated.

Experimental

PP (Koylene M3060, MFI 3 g/10 min) was supplied by IPCL, Vadodara, India and LCP (Vectra A130 (30 wt% of glass fiber filled)) was purchased from Hoechst Celanese, USA. The LCP will be termed as LCP-g in the text. The

Table I. Blending Ratios and Sample Notions

Ingredients	L_{10}	L_{20}	L_{40}	L_{50}	L_{60}	L_{80}
PP	90	80	60	50	40	20
LCP-g	10	20	40	50	60	80

LCP has the comonomer composition of 75 mole% of hydroxybenzoic acid (HBA) and 25 mole% of hydroxy-naphthoic acid (HNA).

Blends of LCP-g with PP were prepared in a Brabender Plasticorder PL 2200(Mixer-N50E) with rotor speed of 30 rpm at the mixing temperature 295 °C for 10 min. The molded slabs were prepared in compression molding at 200 and 300 °C for 8 min. Finally the molded sample was cut into required shape for investigation of different properties. Table I lists the samples prepared in this work.

X-ray diffraction was done with the help of PW 1840 X-ray diffractometer with copper target (Cu-K$_\alpha$) at a scanning rate of 0.05°2θ/sec, Chart speed 10 mm/°2θ, Range 5,000 c/s, T.C. 1 sec. and a slit of 0.2 mm, applying 40 kV, 20 mA, to assess the change of crystallinity of the blends as affected by blend ratios. The area under the crystalline and amorphous portion was determined in arbitrary units. The degree of crystallinity X_c and the amorphous content, X_a was measured, using the following relationships.[16,17]

$$X_c = I_c/[I_a + I_c] \qquad (1)$$

$$X_a = I_a/[I_a + I_c] \qquad (2)$$

Where, I_c and I_a are the integrated intensities corresponding to crystalline and amorphous hollow, respectively.

Peak half width (β), crystallite size(P), interplanar distance(d) were calculated as follows.[16]

$$\beta = \text{Area of the peak / Height of the peak} \times 1/5 \qquad (3)$$

$$P = 79.79/\beta \cos \theta \qquad (4)$$

$$d = 1.548/2 \sin \theta \qquad (5)$$

Thermal analyses were carried out using Stanton Redcroft STA-625 thermal analyzer, in the temperature range of 25-600 °C at a heating rate of 10 °C/min in argon to study the thermal behavior.

Viscoanalyzer-VA-4000 (Metravib RDS) was used to measure the dynamic parameters like storage modulus, loss modulus, stiffness and tan δ within the temperature range of 20 to 200 °C.

Dynamic fracture mechanisms of the blends were studied by Scanning Electron Microscope (JSM-5800 of JEOL Co.), after auto sputter coating of the surface with gold at 0° felt angle. Rheological parameters were studied with the help of

Dynamic analyzer RDA-II (Rheometrics Inc.,USA) equipped parallel plate.

Results and Discussion

X-ray Diffraction Analysis. X-ray diffraction (XRD) diagram of various samples were displayed in Figure 1 and the respective parameters were shown in Table II. The pure PP and LCP-g showed 70 and 30% crystallinity, respectively. In the case of blends, the percent crystallinity increased up to 10% level of LCP-g and then decreased with increasing amount of LCP-g in the blend. The initial increase in crystallite size at the lower level of LCP-g because of enhancement in crystallinity suggested the predominant growth of crystal domain. The characteristic peak of PP at θ_2 was absent in all the concerned blends. This may be due to merging of (040) crystal plane with (130) crystal plane in the blends,[18] although no essential change takes place in the structure of PP from α- to β-or γ- form by the incorporation of LCP-g because of no interaction between the components. LCP-g showed a peak at an angle at θ_5 and which was found to be present in all the blends. With increase in the amount of LCP-g in the blends the intensity of the θ_5 peak was also increased. From 20% and beyond of LCP-g the decrease in crystallinity is associated with decrease in crystallite size at (110) to (130) planes although slight increase in crystallite sizes are observed at (041) and (111) planes. The phenomena suggested the dominating effects of (110) to (130) crystal planes towards
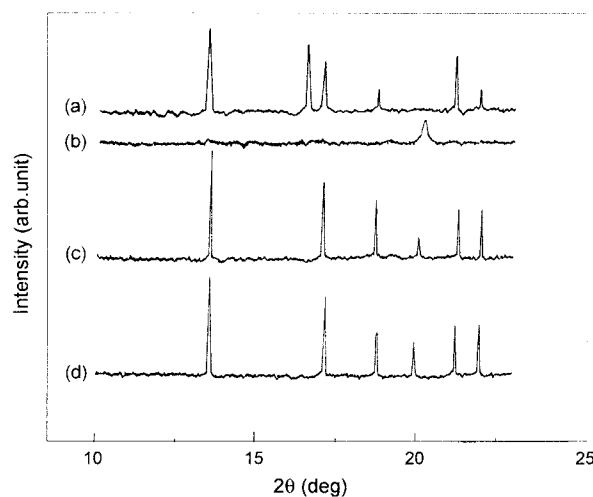

Figure 1 X-ray diffractograms of various samples: (a) PP, (b) LCP-g, (c) PP/LCP-g (90/10), and (d) PP/LCP-g (60/40).
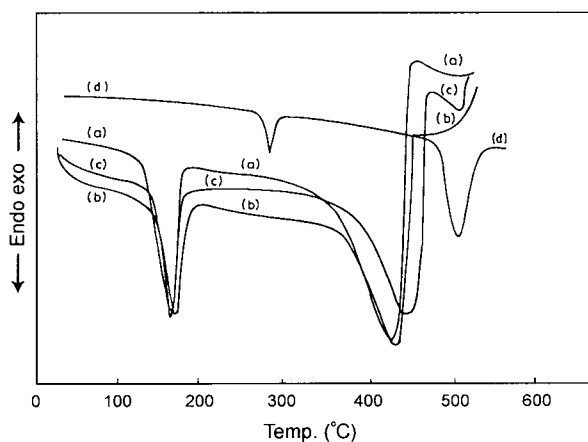
Table II. X-ray Parameters of PP/LCP Blends

| Sample	% Crystal-linity	Peak Angle (2θ in degree) The Numbers in Bracket are the Crystalline Planes*							Interplanar Distance (Å)							Crystallite Size (Å)						
		θ_1 (110)	θ_2 (040)	θ_3 (130)	θ_4 (131)	θ_5	θ_6 (041)	θ_7 (111)	d_1	d_2	d_3	d_4	d_5	d_6	d_7	p_1	p_2	p_3	p_4	p_5	p_6	p_7
PP	70	13.4	16.5	17.0	18.7	-	21.2	21.9	6.63	5.39	5.23	4.76	-	4.20	4.07	91	182	137	138	-	156	138
LCP-g	30	-	-	-	-	20.1	-	-	-	-	-	-	4.43	-	-	-	-	-	-	71	-	-
L_{10}	73	13.5	-	17.0	18.7	19.9	21.2	22.0	6.58	-	5.23	4.76	4.47	4.20	4.05	136	-	156	183	98	138	146
L_{20}	70	13.5	-	17.0	18.8	20.0	21.2	21.8	6.58	-	5.23	4.74	4.45	4.20	4.03	131	-	152	175	95	141	142
L_{40}	59	13.5	-	17.1	18.8	20.0	21.2	21.9	6.58	-	5.20	4.74	4.45	4.20	4.07	119	-	160	173	90	152	153
L_{60}	51	13.6	-	17.0	18.9	20.1	21.1	21.9	6.54	-	5.23	4.71	4.43	4.22	4.07	105	-	148	161	110	135	138

* Taken from Ref. 18.

the crystallinity of the blends. As evident from the table, however, the interplanar distances of the various samples were almost unchanged.

Thermal Analysis. To study the decomposition pattern and thermal stability of the PP/LCP-g blends, differential scanning calorimetry (DSC)/thermogravimetric analyzer (TGA) measurements were carried out. The DSC/TGA plots of the samples were displayed in Figures 2 and 3 and

the respective parameters were shown in Table III. The DSC/TGA para-meters were determined by using Stanton Redcroft thermal analysis software.

From Table III, it was observed that the heat of fusion was highest for 10% LCP-g containing blend and then decreased

Figure 2. DSC plots of the blends. (a) PP, (b) PP/LCP-g (90/10), (c) PP/LCP-g (60/40), and (d) LCP-g.
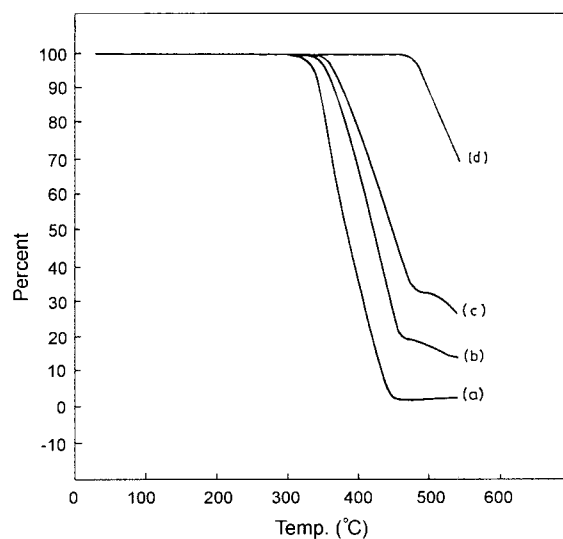
Figure 3. TGA plots of the blends. (a) PP, (b) PP/LCP-g (90/10), (c) PP/LCP-g (60/40), and (d) LCP-g.

Table III. DSC/TGA Parameters of PP/LCP Blends

Sample	1st Decom. Temp. (°C)	Loss of Wt. (%) for 1st Step.	T_m (°C)	ΔH_f (cal/g)	Heat of Decomposition (1st step) H_1 (cal/g)
PP	327	97	166	19.06	84.78
L_{10}	342	86	167	20.56	71.07
L_{20}	345	79	165	17.67	67.52
L_{40}	352	66	164	14.01	61.40
L_{60}	360	54	163	12.21	54.25
L_{80}	369	45	161	11.05	49.31

with higher amount of LCP-g present in the blend system, which was supported by the XRD results. Pure PP showed a melting endotherm, T_m, at about 166 °C whereas for LCP-g it occurred at about 282 °C. The melting endotherm of blends showed values close to the T_m of PP. At 20% level of LCP-g and beyond, the melting temperature of PP marginally decreased due to the dilution effect. The TGA plot revealed that one step decomposition occurred in case of pure PP and two step decomposition occurred in case of the blends. In the case of pure PP early decomposition occurred at 327 °C with 97% loss in weight in this step. Whereas for the blend L_{10} the decomposition delayed and started at 342 °C and the 86% sample was decomposed. As observed, the first as well as second decomposition temperatures shifted towards the higher temperature side and lower amount of sample was decomposed with increasing amount of LCP-g in the blend. So, thermal stability of the blends was enhanced by the addition of LCP-g in PP.

The heat of decomposition associated with first decomposition was highest for PP and decreased with increasing amount of LCP-g in the blend with PP. It is well known that endothermic peak suggested the absorption of heat from outside. Hence, lower amount of heat of decomposition means larger decomposition, assuming the reaction to be an endothermic. So, from the thermal parameters it can be concluded that the decomposition starts at higher temperature in case of blends, but the decomposition was rapid in these cases. Here again for pure PP, decomposition started earlier, but the process was slower compared to all the blends for first step of decomposition.

Dynamic Mechanical Analysis. The dynamic mechanical properties like dynamic modulus, loss modulus, stiffness and tan δ were studied of the samples molded at 300 °C. The dynamic mechanical thermal analyzer (DMTA) parameters (glass transition temperature, β-transition and α' relaxation) were calculated from variation of tan δ with temperature curve for the blends and represented in Table IV. From the table it was observed that the glass transition temperature of all blends was around 105 to 108 °C which corresponds to that of LCP-g. Other relaxation transition can be found on the lower temperature side (50-55 °C of the primary relaxation). This was secondary relaxation i.e. β-transition of

Table IV. DMTA Parameters of PP/LCP Blends

Blend No.	α-Peak Temp.(°C) [from tan δ]	β-Peak Temp.(°C) [from tan δ]	α'-Peak Temp.(°C) [from tan δ]
L_{20}	108	55	185
L_{40}	107	54	185
L_{50}	106	54	186
L_{60}	106	53	187
L_{80}	105	50	187

LCP-g. This lower temperature transition was a short range relaxation which was attributed to the relaxation of the naphthyl units of the HNA monomers, as in earlier works.[19,20] Peaks around 185-187 °C may be assigned to the α' relaxation which was very much prominent in case of LCP-g rich blend (L_{60} & L_{80}). This type of relaxation generally occurred in case of highly crystalline polymer between the T_g and T_m hence it could be α' relaxation of LCP-g. This relaxation had been attributed to molecular motion within the crystalline phase.[21]

Figures 4a, b and c showed the variation of stiffness, dynamic modulus and loss modulus as a function of LCP-g concentration at different temperature and frequency. From the figures it was observed that the dynamic modulus, loss modulus and stiffness increased with LCP-g content up to around 50% LCP-g and then decreased as its higher level. A clear inflection point was observed at around 50% LCP-g level in the blend. It is quite clear from these studies that beyond 50% of LCP-g, the slope changes indicate the phase inversion, with probably a co-continuous phase at around 50% LCP-g in the blend. Considering the presence of 30% glass fiber in the LCP-g, the phase inversion can be considered at 35% of pure LCP in the blend with PP. This phenomenon was probably independent of the frequency applied.

SEM Study. The study of fracture mechanism was carried out on dynamically fractured surface of the samples. The sample was taken out after failure at 200 °C was observed and the fracture surface was then scanned after gold coating and were represented in Figures 5(a and b). The SEM photographs suggested that the creation of voids and destruction of the fibrills during DMTA analysis. At the lower level of LCP-g (Figure 5a) the microphotograph was characterized by matrix flow of low melting PP. The voids were due to the layer separation of matrix phase and removal of glass fiber (in LCP-g) under the dynamic condition. However, at higher level of LCP-g (L_{50}) the fiber breakage was prominent with lower level of matrix flow. Fiber formation could be observed in both cases. But, blend L_{50} showed higher amount of fiber than L_{20} (lower level of LCP-g in the blend).

Rheological Characterization. Flow behaviors of the blends L_{10}(PP/LCP-g = 90/10)and L_{40} (PP/LCP-g = 60/40) have been studied at 200 and 300 °C over a low shear rate region(between 0.1 and 100 s^{-1}). Two temperatures were selected to study the overall melt processability (300 °C) and also to study the effect of LCP-g fibrils and crystallinity on the PP melt (at 200 °C). Slabs were also made at two different temperatures viz 200 and 300 °C in order to study the effect of microstructural changes on the rheology of the blends. Figures 6 and 7 represented the variation of the viscosity with shear rate. At both the temperatures of study the viscosity decreased with the shear rate but with two distinct slopes varying its pseudoplasticity at a limiting shear rate of 25-30 s^{-1} (Figures 6a and b) particularly when the molding temperature is high (300 °C). However, no such trend is observed in
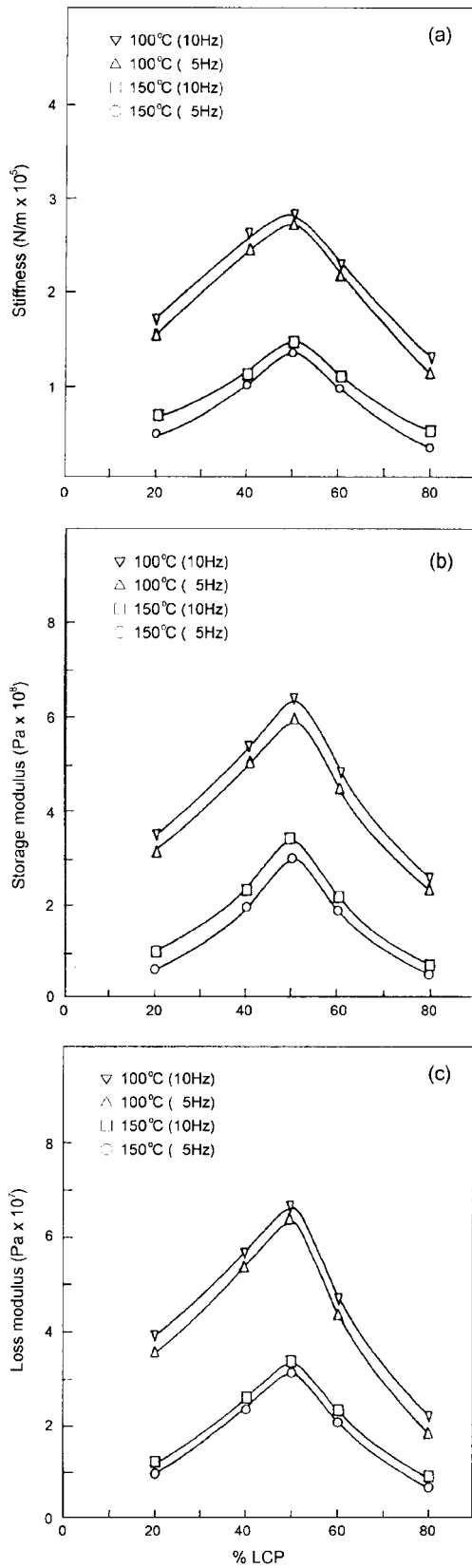
Figure 4. Variations of (a) stiffness, (b) storage modulus, and (c) loss modulus against blend ratios at different temperatures.
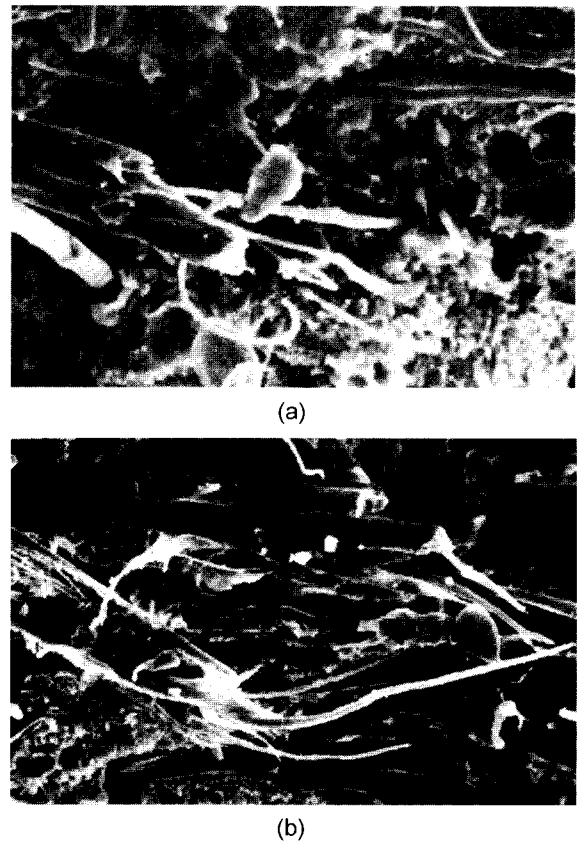

(a)

(b)

Figure 5. SEM photograph of the blends [1000 ×]; (a) PP/LCP-g (80/20) and (b) PP/LCP-g (50/50).
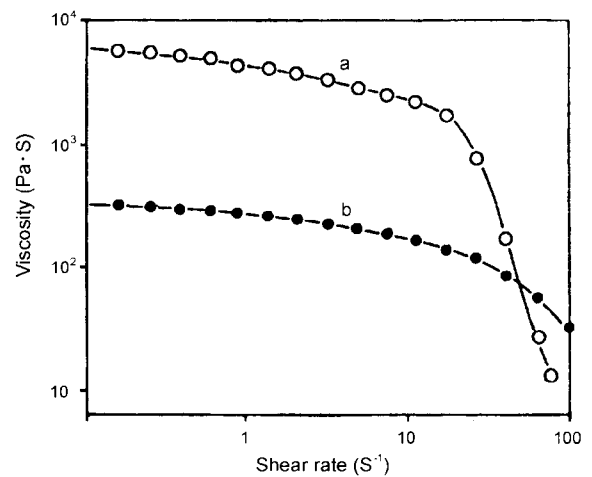

Figure 6. Variation of viscosity with shear rate for PP/LCP-g = 90/10 molded at 300 °C, studied at 200 °C (a) and PP/LCP-g = 90/10 molded at 300 °C, studied at 300 °C (b).

the case of higher LCP-g containing blends (L_{40}, Figures 7a and b), irrespective of the molding temperatures employed. Instead, the L_{40} blend having higher LCP-g concentrations
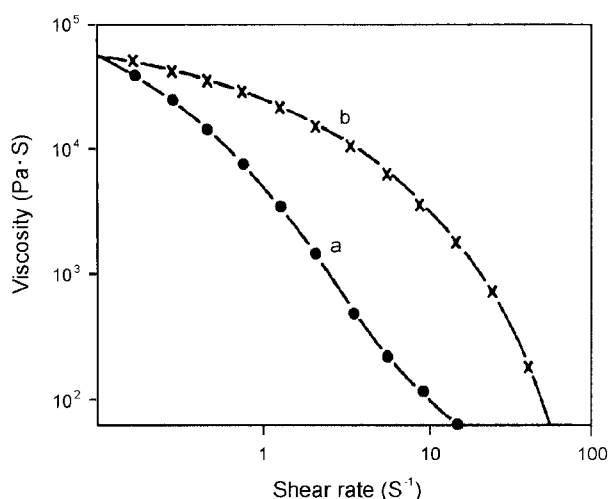
Figure 7. Variation of viscosity with shear rate for PP/LCP-g = 60/40 molded at 300 °C, studied at 200 °C (a) and PP/LCP-g = 60/40 molded at 200 °C, studied at 200 °C (b).

shows a typical yielding behavior at lower shear rates due to the presence of LCP-g. At lower temperature of testing (200 °C), the increase in LCP-g increased the viscosity of the blend. It is noteworthy that the low temperature of molding (200 °C) is associated with higher viscosity, for a particular blend ratio, when studied at the low temperature, same as molding (200 °C) temperature than when studied at high temperature (300 °C). The interesting phenomena may be due to the microstructural changes occurring in the blend systems depending on the molding temperature whether it is nearer to either the melting temperature of PP or the melting temperature of LCP-g.

It has been found out that the molding temperature has a remarkable effect on the crystal domain formation in this type of blend, in part due to heterogeneous crystallization under different cooling rates. For L_{40} blend the slab made at 200 °C is having higher crystallinity (heat of fusion 65.1 J/g) than the slab made at 300 °C (heat of fusion 54.2 J/g). It is worth mentioning that when the slab is molded at 200 °C the PP phase is in the molten state and the nucleation is started from the crystal domain of LCP-g already existing in the system. While the slab is made at 300 °C, both the phases are in molten state and probably co-crystallization exist while forming the crystals during cooling may be due to pseudo-homogeneous crystallization. Molding at 200 °C gave rise to higher crystallinity with lower crystallite size. However molding at 300 °C is associated with lower crystallinity and higher crystallite size. Hence, it can be logical to assume that at molding temperature of 200 °C the nucleation is favored, while at 300 °C molding temperature the growth is predominant. These observations are quite in agreement with the findings by Ha et al.[22,23] while using sodium benzoate as nucleating agent for PP. They suggested the improved

nucleating effect of sodium benzoate in PP is due to its polar groups and heterogeneous crystallization.

Conclusions

Higher percent crystallinity was observed with lower level of LCP-g (10%) in the blend with PP. The thermal stability of the blends was found to be better in comparison to the pure PP. Phase inversion occurred at 50% LCP-g in the blend. Considering the 30% glass fiber content in the LCP-g it can be logical to assume the phase inversion at 35% level of pure LCP in the blend with PP. Under dynamic application, the matrix flow was restricted at the higher level of LCP-g content. Molding at the melting temperature of PP gave rise to higher crystallinity of the blend which is associated with higher viscosity when studied the rheology also at the melting temperature of PP. Heterogeneous crystallization seems to be highly effective in PP/LCP-g blends.

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