Theoretical Analysis and Experimental Study on Microfibrillar Morphology Development in PP/TLCP Blend

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ABSTRACT

In this paper it has been demonstrated that it is possible to generate in situ fibre composite from blends of a thermotropic liquid crystalline polymer (TLCP) and polypropylene by using combination of a modular multi-fed twin-screw extruder with an extensional flow mixer (EFM) as a novel process. Experimental results revealed that almost all TLCP droplets passing through the converging-diverging regions of the EFM are deformed into fibrils oriented to flow direction, indicating that this process does not suffer the limitation imposed by viscosity ratio of the blend components and TLCP concentration. The results obtained from the flow analysis performed on the converging regions of the EFM showed that L/D distribution of the TLCP fibrils can be predicted in terms of the lineal stretch parameter calculated on the basis of kinematical approach.

Key Words: liquid crystal polymer, morphology, microfibril, in situ fibre composite, extensional flow mixer, lineal stretch

INTRODUCTION

In recent years, the blending of thermotropic liquid crystalline polymers (TLCP) with thermoplastics has been the focus of intense academic and industrial interest [1-12]. This interest is mainly focused on the fact that under appropriate melt processing condition the TLCP dispersed phase can be deformed into fine oriented fibrils, which upon solidification acts to reinforce the matrix. Since, such oriented fibril-matrix morphology is generated during the process, resulting in blends with higher mechanical properties compared to those with spherical morphology, these blends are often referred as in situ composites. In addition TLCPs can improve the processability of the matrix polymers because of their low viscosity under processing conditions [1-5].

In the conventional method, the required fibril-matrix morphology for in situ composites is commonly generated with conventional dispersing mixing equipment like single and twin-screw extruders. In these processing techniques the TLCP is first dispersed as fine droplets which are elongated into microfibrils in a subsequent extensional flow steps and finally frozen-in upon solidification. It has been recognized that, application of strong extensional...
flow in the final stage of processing established in converging die or by drawing outside the die are necessarily not only for the formation of high aspect ratio TLCP fibres but also to induce a high degree of molecular orientation in the fibres [2, 3, 13-16]. Champagne et al. [17] demonstrated that the fibre content of the in situ composites increases with increasing the draw ratio to some extent above which, depending on the TLCP concentration, it remained unchanged.

The mechanism by which high aspect ratio oriented fibrils are formed in blends of TLCPs and thermoplastics is still uncleared. This is because many factors such as hydrodynamic forces, rheological properties of the blends components, interfacial forces between phases, mixing history and TLCP concentration can play a role in generating fibril-matrix morphology and final microstructure of the blends. Contribution of many of these parameters on development of reinforcing TLCP fibrils in resultant blend has been studied by a number of researchers who have reported several contradictory findings [14-19].

It has been reported that the viscosity ratio of the components can have a great influence on the fibril/matrix formation of these blends [20-25].

There have been several reports focused on the effect of TLCP concentration on generating the fibril/matrix morphology [26]. The role of TLCP concentration on process of in situ fibre formation from droplet/matrix dispersion can be qualitatively described using the theory of deformation and droplet break up originally developed by Taylor [20]. Accordingly, for each blend system there is a certain minimum TLCP concentration below which the TLCP droplet size produced in the melt blending step becomes so small that the viscous stresses imposed during processing can not overcome interfacial forces and, therefore, the TLCP droplets do not form fibrils.

At increasing TLCP concentration, the fibre formation tends to be easier due to the presence of larger TLCP droplet size which can easily be deformed into fibrils in an extensional flow field.

In contrast with conventional in situ composite process, a novel dual extrusion process has been developed by Baird and his co-workers [27-30] in which the TLCP fibrils are not generated from dispersed droplets but are formed by a mainly distributive mixing in the actual melt blending process. In this process, the TLCP and matrix are plasticated in two separate extruders before mixing in a series of static mixing elements. The static mixing elements act as distributive mixing, operating by repeated splitting, stretching and recombining the polymer melt streams. A similar process has been used by Machiels et al. [23] for several blends containing TLCP.

In the present work an attempt has been made to use an extensional flow mixer (EFM), combined with a co-rotating multi-fed twin-screw extruder, as a novel process to produce in situ fibre composites. Special attention has been made to determine if this process can be utilized to generate a fibrillar TLCP morphology from blends having viscosity ratio greater than unity, the result which can not be obtained by direct melt blending in extruders.

EXPERIMENTAL

Materials

The thermotropic liquid crystalline polymer (TLCP) used was Vectra A 950 supplied by Celanese. The Vectra A 950 is an aromatic random copolyester consisting of 73% 4-hydroxy benzoic acid (HBA) and 27% 2-hydroxy-6-naphthoic acid (HNA). It has exhibited a crystalline to liquid crystalline transition at 285 °C, as measured with DSC in the first heating scan. The second heating scan, after quenching from the liquid crystalline melt, revealed a melting point of 280 °C. The polypropylene as a matrix material was a homopolymer with melt flow index of 4 g/10 min at 210 °C and $M_w = 450,000$ supplied by Himont Co.

Extensional Flow Mixer

An extensional flow mixer (EFM) with characteristics almost similar to that introduced by Utraki [31] was constructed and fitted to a co-rotating modular multi-fed twin-screw extruder (Brabender TSE 25). A schematic representation of the EFM used in this work is shown in Figure 1. For more details see ref.
In this device the molten polymers enter the EFM from the TSE through an adapter. The melt is smoothly distributed to slits located between cone and the mounting ring. Next the melt enters the annular space inside the EFM body, flows towards the center which undergoing convergent and divergent (c-d) regions before sorting out through the central bore and the fitted circular.

**Blend Processing**

Blends of Vectra A950 and PP were produced using a co-rotating twin-screw extruder (TSE 25) combined with an extensional flow mixer (EFM). The TLCP was fed to the extruder by means of an adjustable dozing feeder. The PP was fed into the molten TLCP through the second dozing feeder. This method of feeding was used in order to reduce PP residence time in extruder and therefore minimizing the PP thermal degradation. Maximum temperature of the melting zones of the twin-screw extruder and the EFM was set to 290°C. The composition of the blend materials was closely monitored and maintained during the process by adjusting the rate of the dozing feeders. A number of blend samples were also produced by direct blending in TSE fitted with a capillary but without using the EFM, in order to evaluate the efficiency of the EFM. All blend samples were quenched in cold water in order to prevent additional stretching. The blend samples were produced at constant temperature but at different extensional deformation imposed in the EFM, which could be manually adjusted by the EFM gap setting and monitored by means of a pressure transducer fitted into the adapter. In this work results obtained from three sets of blend samples, all containing 20 wt% TLCP but produced using different processing conditions, have been reported. These include blend samples produced by direct blending, a sample produced using the EFM in the process at pressure equal to 50 bar and a sample produced using EFM at pressure equal to 100 bar. All samples were produced at constant screw speed of 120 RPM.

**Morphology Study**

The morphology of the blend was studied using scanning electron microscopy technique (SEM 360 Cambridge Instrument). The SEM samples were prepared by cryogenic fracture after immersion in liquid nitrogen for at least 10 min. The fractured samples were fixed to aluminium stubs and coated with a layer of gold to enhance conductivity.

**RESULTS AND DISCUSSION**

**Morphology**

Scanning electron micrograph shown in Figure 2 represents morphology of the core region of fracture surface of the extruded sample produced by direct blending in twin-screw extruder (simple mixing). The TLCP phase is in the form of spherical droplets.
dispersed in the PP matrix. The TLCP particles pulled out of the matrix during fracture, as evidenced by the holes left in the matrix, indicating that interfacial adhesion between the two phases is poor.

Figure 3 shows the SEM micrograph of a part of cross section of the same extruded sample. A pronounced skin layer observed for this sample indicates that for the sample produced by simple blending process; some of the TLCP phase tends to migrate toward the die wall forming a continuous skin layer. Similar skin-core morphology has also been reported by other researchers using simple blending process [27].

Figure 4 shows SEM micrograph of fracture surface of the extruded blend sample produced using combination of TSE and EFM at $\Delta P=50$ bar. Close examination of this micrograph revealed that for this sample almost all TLCP droplets are deformed into fibrils, which are oriented in the flow direction. As can be observed in Figure 5, in this sample the TLCP fibrils are well distributed through extruded cross section with no appreciable skin effect.

Figure 6 shows the SEM of a sample which was produced using the same processing condition as that used for the former sample with only increased extent of extensional rate imposed in EFM ($\Delta P=100$ bar). From comparing this micrograph with that shown in Figure 4, it can be found that increasing the extent of
The extensional rate of deformation imposed in the EFM increases the extent of the TLCP fibrillation and therefore, it has an enhancing effect on generating the in situ fibre composites.

Finally, the uniform L/D distribution of the TLCP fibrils observed for the blend samples produced using EFM reveals that, there is a strong correlation between the size of TLCP droplets produced in TSE and the dimension of the fibrils generated in the EFM.

**Modeling**

In this part of our work an attempt has been made to estimate the aspect ratio (L/D) of the TLCP fibrils and their L/D distribution over extrudate cross section in terms of the lineal stretch (λ) on the basis of kinematical concepts and make a qualitative comparison between these parameter and experimental results. The reason for doing this flow analysis was that, from the above experimental results it seems that almost all TLCP droplets passing through the converging regions of the EFM are deformed into the fibrils, which do not undergo any breakage. For this purpose a dihedron converging flow field described in Figure 7 has been considered as one of its EFM converging zones.

It has been shown that [32] for such region the rate of deformation tensor (D) and component of velocity field (v) can be given as follows:

\[
D = \begin{bmatrix}
0 & 0 & 0 \\
0 & -\dot{\varepsilon} & \dot{\gamma} \\
0 & \dot{\gamma} & \dot{\varepsilon}
\end{bmatrix}
\]  

\[
v_x = 0, \quad v_y = \dot{\gamma}z - \dot{\varepsilon}y, \quad v_z = \dot{\gamma}z + \dot{\varepsilon}y
\]  

Where, \(v_i\)'s are the components of velocity vector; \(v\), \(\dot{\gamma}\) and \(\dot{\varepsilon}\), are the extension and shear rates of deformation, respectively. In this case the components of the position vector \(x = x(0)\) can be obtained from the equation \(x_t = x_0 + \dot{x}_0 t\), dt considering their initial values \(x_0 = x(0)\) where \(x_0\)'s are the components of position vector at time \(t=0\) and \(x_0\)'s are the components of position vector at time \(t\), which at its maximum level equals to element residence time, thus:

\[
x = x_0; \quad y = y_0 + \gamma z - \varepsilon y; \quad z = z_0 + \gamma z + \varepsilon y
\]  

Where \(\gamma, \varepsilon\) are the total extensional and shear deformation at time \(t\), respectively. By differentiating \(x_t\)'s with respect to \(x_0\)'s we can obtain components of deformation gradient tensor, \(F\), defined as \(F_{ij} = \frac{\partial x_i}{\partial x_0}\) therefore:

\[
F_{xx} = 1; \quad F_{yy} = F_{xz} = (1 - \varepsilon)(1 - \varepsilon^2 - \gamma^2); \\
F_{xy} = [(1 - \varepsilon)(1 + \varepsilon)]{\gamma/[(1 - \varepsilon)^2 - \gamma^2]}; \\
F_{xz} = (1 + \varepsilon)[1 - (\varepsilon^2 + \gamma^2)]; \text{ others equal to zero. (4)}
\]

The deformation gradient tensor and its transpose can be combined to yield the right relative Cauchy-Green strain tensor \(C\) as \(C_{ij} = F_{ij}^T F_{ij}\), therefore the non-zero component of \(C\) may be as follows:

\[
C_{xx} = 1; \quad C_{yy} = [(1 - \varepsilon)^2 + \gamma^2]/(1 - \varepsilon^2 - \gamma^2)^2; \\
C_{yz} = C_{xy} = 2(1 + \varepsilon)^2\gamma/[(1 + \varepsilon)(1 - \varepsilon^2 - \gamma^2)^2]; \\
C_{zz} = [(1 + \varepsilon)^4 + \gamma^2(1 - \varepsilon)^2]/[(1 + \varepsilon)^2(1 - \varepsilon^2 - \gamma^2)^2]
\]  

By considering \(\lambda^2 = C_{ii} m_0 m_{oi}\), the lineal stretch can be calculated as follows:

\[
\lambda = \{(1 + \varepsilon)^4 + \gamma^2(1 - \varepsilon)^2]/((1 + \varepsilon)(1 - \varepsilon^2 - \gamma^2)^2))^{1/2}
\]  

Since the extent of \(\varepsilon\) and \(\gamma\) vary depending on position (x), geometrical factor and processing conditions (pressure drop and flow rate; \(\Delta P, Q\)), the \(\lambda\) will have a distribution over any cross section of flow field. Our main objective was to predict the distribution of \(\lambda\) on the cross section A-A as shown in Figure 7. The eqn (6) can be solved using following assumptions:

- The TLCP droplets sizes are too small compared with the gap of cross section A-A.
- All TLCP droplets passing through the converging region are deformed to fibrils with no break-up.
- Influence of the diverging regions on deformation

\[x = x_0; \quad y = y_0 + \gamma z - \varepsilon y; \quad z = z_0 + \gamma z + \varepsilon y \]  

Where \(\gamma, \varepsilon\) are the total extensional and shear deformation at time \(t\), respectively. By differentiating \(x_t\)'s with respect to \(x_0\)'s we can obtain components of deformation gradient tensor, \(F\), defined as \(F_{ij} = \frac{\partial x_i}{\partial x_0}\) therefore:

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F_{xx} = 1; \quad F_{yy} = F_{xz} = (1 - \varepsilon)(1 - \varepsilon^2 - \gamma^2); \\
F_{xy} = [(1 - \varepsilon)(1 + \varepsilon)]{\gamma/[(1 - \varepsilon)^2 - \gamma^2]}; \\
F_{xz} = (1 + \varepsilon)[1 - (\varepsilon^2 + \gamma^2)]; \text{ others equal to zero. (4)}
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- The TLCP droplets sizes are too small compared with the gap of cross section A-A.
- All TLCP droplets passing through the converging region are deformed to fibrils with no break-up.
- Influence of the diverging regions on deformation
of the TLCP droplets is assumed to be negligible. TLCP and PP both exhibit power law behaviour in the extensional and shear flow [29-31]. Thus by considering the rheological, geometrical and operating parameters (ΔP, Q), it is possible to predict ε and γ [32] and therefore, the lineal stretch (λ) distributions on the cross section A-A in the Figure 7.

In order to apply the above concept to the EFM which has P successive similar converging regions, the total lineal stretch (λP) can be calculated on the basis of the lineal stretch evaluated for a single converging region as discussed above using the following relation:

$$\lambda_P = (\lambda)^P$$  \hspace{1cm} (7)

Figure 8 shows the distribution of λP (L/D) over

![Figure 8](image_url)

Figure 8. The lineal stretch (λ) distribution predicted for the A-A cross-section of the last converging region of EFM at three different pressure and Q=1000 cm³/hr.

The above predicted results also suggest that the L/D of TLCP fibres increase with increasing ΔP.

CONCLUSION

It has been demonstrated that the in situ fibre composites from TLCP/PP blends can be generated by using the combination of a co-rotating modular multi-fed twin-screw extruder (dispersive mixer) and an extensional flow mixer (fibrils generator) as a novel process.

Experimental results revealed that this process does not suffer from the limitations imposed by viscosity ratio of the blends components and the TLCP concentration with no need for post-drawing of extrudates. Flow analysis performed on the EFM suggests that the L/D distribution of the TLCP fibrils generated in the EFM can be predicted in terms of the total lineal stretch (λP) calculated on the basis of kinematics concept.

REFERENCES