Rheological Hybrid Effect and its Conditions in Filled Polymer Melts

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Summary: In contrast to usually increased viscosity of filled polymer melts with increasing filler content, some filled polymer melts showed decreased melt viscosity in the presence of thermotropic (main chain) liquid crystalline polymer (LCP) with increasing filler content. This phenomenon was termed as rheological hybrid effect and found correlated well with the fibrillation of LCP melt droplets. Investigation of this LCP fibrillation in matrix polymers, with fillers of various shapes at micro- and nano-meter scales, showed that LCP fibrillation was promoted by the filler addition, depending upon thermodynamic and hydrodynamic driving forces involved.

Keywords: composites; fillers; liquid-crystalline polymers (LCP); morphology; rheology

Introduction

Usually fiber-reinforced or particulate-filled polymer melts have increased viscosity compared to their corresponding matrix polymer melts. This tendency has been predicted by Kitano and coworkers[1] and summarized by Metzner.[2] In spite of the aspect ratio of fillers, the relative viscosity of filled polymer melts is always higher than that of their corresponding pure matrix melts and increases with increasing filler load.

However, in contrast to this tendency, in the study of in-situ hybrid composites[3,4] it was found that some polymer melts with added fillers and thermotropic liquid crystalline polymer (LCP) had a decreased melt viscosity compared to their neat polymers and those filler-loaded or LCP-blended, and had an even more decreased viscosity with increasing filler loading. Based on our concept and previous journal publications, this review article is going to give a general description of this kind of phenomenon and summarize its conditions in filled polymer melts. Due to the different sources of these publications, the denotation of ternary composite systems is sometimes not uniform, especially in the cited figures.

Rheological Hybrid Effect

For a clearer understanding of these phenomena it is better to start with a new technical term: rheological hybrid effect.[5] Its definition is as follows: ‘‘a phenomenon in which the melt viscosity of a ternary polymer blend decreases with increasing filler loading, influenced by the minor polymer phase in the blend’’.

This effect was observed in several ternary blend or composite systems. Taking spherical glass bead (GB) as the filler, ternary Nylon 6 (N)/GB/Vectra A950 (an aromatic copolyester used in all of these correspondingly cited papers, and simplified to LCP in the context for convenience) composites were obtained.[5] Although the ball bearing effect worked at lower GB filling as occurred in polycarbonate (PC)/GB composites,[6] this ball bearing effect did not work at higher GB filling. The viscosity of binary N/GB composites increases with increasing bead content over the entire range of shear rate investigated, such as $\eta_{(\mathrm{N/GB1})\ (45/55)} > \eta_{(\mathrm{N/GB1})\ (62/38)} > \eta_{(\mathrm{N/GB1})\ (95/5)}$ at shear rate of 115.2 s^{-1}

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(Figure 1). However, the viscosity of ternary N/GB/LCP composites is quite different from that of binary N/GB composites. At lower shear rate, the higher the bead content is, the lower the viscosity, such as $\eta_{(N/GB1/LCP)\ (84/5/11)} > \eta_{(N/GB1/LCP)\ (51/38/11)} > \eta_{(N/GB1/LCP)\ (34/55/11)}$. This trend goes up to 55 wt% of glass bead loading. In addition, over the entire range of shear rate, the viscosity of ternary N/GB/LCP composites is lower than that of neat nylon, LCP, binary N/LCP blends and N/GB composites. At the shear rate of 1152 s^{-1}, viscosities of ternary N/GB/LCP composites with 38 wt% and 55 wt% of glass bead are only 8% and 12% of neat nylon 6, respectively. The addition of glass bead decreases the viscosity of nylon 6/GB/LCP composite melts up to 55 wt% of glass bead loading (Figure 2). This rheological hybrid effect was also observed with the same composite systems containing glass beads of different diameters. Interestingly it was found that this viscosity decrease of these ternary composites correlated well with the fibrillation of LCP melt droplets (Figure 3).

Another typical example was nano-SiO_2-filled bisphenol-A polycarbonate (PC)/Vectra A950 blend.[7] The resulting PC/SiO_2/LCP composites also exhibited rheological hybrid effect. It is seen from Figure 4 that with increasing nano-SiO_2 content from 1 to 10 wt%, the relative shear viscosity of the binary PC/SiO_2 composites increases from 1.10 to 1.50 at 70 s^{-1}, and from 1.0 to 1.24 at 2600 s^{-1}, respectively. The relative viscosity of all the PC/SiO_2 composites is larger than unity and increases monotonously with increasing nano-SiO_2 content at given shear rates. As for the binary PC/LCP blends, their relative viscosity decreased slightly upon the only addition of 10.7 wt% LCP at different shear rates, giving a relative shear viscosity of 0.98 at 70 s^{-1} and 0.84 at 2900 s^{-1}, respectively. However, contrast to the PC/LCP blends, the relative shear viscosity of the PC/SiO_2/LCP composites ($\eta_{TLCP/SiO_2/PC}/\eta_{PC}$) shows an inverse behaviour. It decreases to 0.72 for PC/LCP/Silica (1%) and further to 0.61 for PC/LCP/Silica (10%) at 70 s^{-1}; to 0.56, 0.41 at 550 s^{-1}; to 0.54, and finally to 0.44 at 1250 s^{-1}. At 2900 s^{-1}, the relative viscosity decreased to 0.53 for PC/LCP/Silica 1% and further to 0.46 for PC/LCP/Silica 3%, and slightly increased to 0.51 for PC/LCP/Silica 10%. Here, the slightly increased viscosity at such

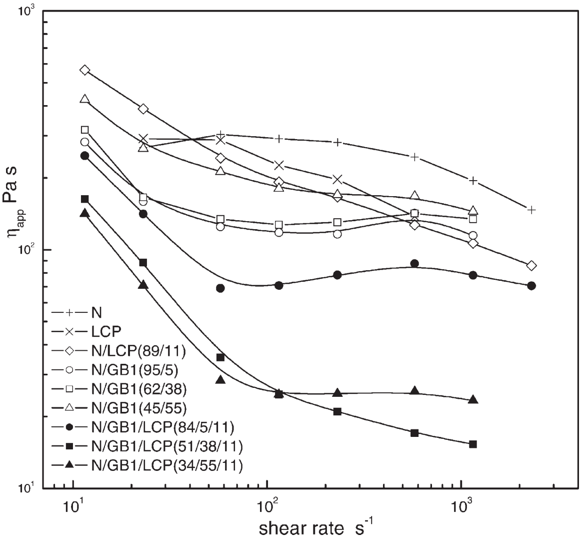

Figure 1.
Rheological curves of binary and ternary composites with different GB contents by weight percentage.[5]

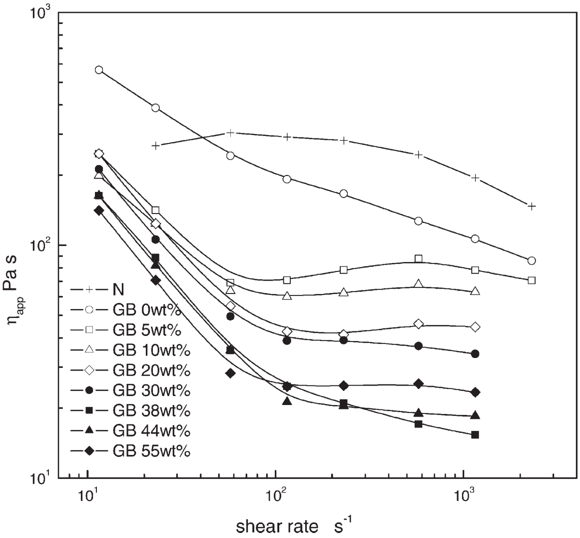

Figure 2.
Rheological curves of ternary polyamide 6 (N)/GB/LCP ((N + GB)/LCP = 89/11) composites with different GB weight percentage.[5]

high shear rate might be attributed to the shear-thickening behavior of fumed nano-SiO_2. And the viscosity reduction correlated well with the deformation and fibrillation of LCP droplets (Figure 5) and became even more significant when the deformation and fibrillation was greatly enhanced at relatively high shear rates.

Before the observation of these typical phenomena, this kind of viscosity reduction was first observed in polymer composites with increasing contents of glass fiber in the presence of LCP. For PC/LCP blends reinforced by glass fiber (GF),[8] a hybrid composite with its formulation of PC/GF/LCP 90/5/5 had better flow properties than samples containing no glass fiber such as PC/LCP 95/5 blend. The LCP morphology was one of the important parameters that determined the flow property of the hybrid composite. If the LCP droplets deformed into fibrils, the composite showed an increased flow. If spheres dominated the morphology of LCP domains, the composite had a higher viscosity.

Polyamide 6 (PA6), which was less viscous than Vectra A950, was chosen as the matrix of PA6/GF/LCP in-situ hybrid composites.[9] Surprisingly, it was found that the addition of glass fiber significantly reduced the melt viscosity of PA6/LCP blends. This effect was so marked that some PA6/GF/LCP composites had a quite low viscosity, not only lower than neat PA6,

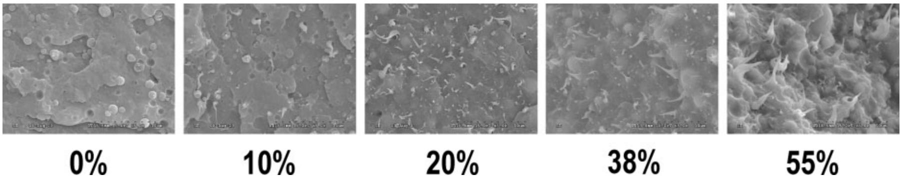

Figure 3.
Morphology of ternary N/GB/LCP composites with different GB contents at shear rate of 115 s^{-1} (LCP content is 11 wt %).[5]

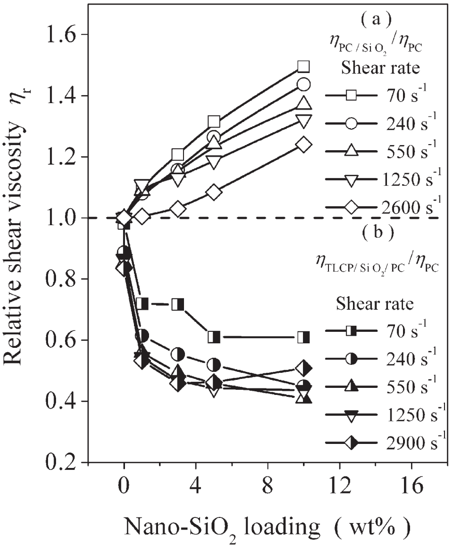

Figure 4.
Effect of nano-SiO_2 loading on the relative shear viscosity of composites at 285 °C: (a) binary PC/SiO_2 composites; (b) corresponding ternary PC/SiO_2/LCP composites with 10.7 wt% LCP.[7]

neat LCP and PA6/GF composites, but also lower than the corresponding binary PA6/LCP blends. The great reduction of the melt viscosity was regarded as the result of LCP fibrillation.

Rheological hybrid effect was observed in ternary polymer systems containing LCP with the addition of glass fiber, glass bead and nano-silica. Their significantly reduced melt viscosity correlated well with the formation of LCP fibrils in these material systems, especially at high filler loading. Actually, the lubrication effect is not caused by LCP fibrils themselves in the solid form. It is the LCP domains highly stretched along the flow direction that lubricates the whole melt system. This conclusion can be drawn from the recently published papers of Gao and her coworker on blends of an LCP and high molar mass polyethylene (HMMPE).[10,11] They have concluded that the chain alignment in the elongated LCP domains causes chain alignment and disentanglement in the neighboring HMMPE melt. The high level of alignment of pure PE is attributed to the stronger interaction between the two constituents during flow caused by molecular alignment and entanglement reduction at the interface. Their experimental observation and phenomenological model supply a basic understanding for the drastic viscosity reductions found to be due to the intimate interactions between the two materials after the LCP domains become highly stretched along the flow direction. During the cooling process of these material systems, these highly elongated LCP domains are frozen to the form of final fibrils due to the long relaxation time of their rigid molecular chains. In summary, the highly elongated LCP domains, which appear in the form of fibrils in resultant materials, play a much effective role to the viscosity reduction of blends or composites than LCP spheres do.

Importantly, these ternary composites had both, increased flow properties and enhanced mechanical performances, with one example as shown in Figure 6.[12] This verified indirectly that the viscosity reduction of these material systems was not contributed by the degradation of matrix polymers having high filler contents. These advantages would

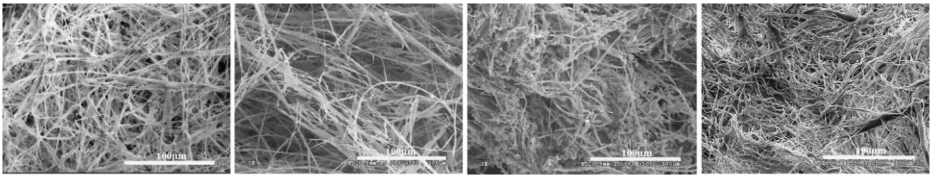

Figure 5.
SEM pictures of flocculated long LCP fibrils extracted from extrudates of PC/SiO_2/LCP composites with varying nano-SiO_2 contents. From the left to right are PC/LCP/Silica 1%, PC/LCP/Silica 3%, PC/LCP/Silica 5% and PC/LCP/Silica 10%, respectively at ca. 550 s^{-1}.[7]

find potential application for engineering plastics and especially advanced engineering plastics such as polyethersulfone, polysulfone and polyetheretherketone.

Multi-scale Effect of LCP Fibrillation

Usually, rheological behavior of polymers in their processing controls the morphology of resultant materials, upon which their mechanical performances depend. In the present study of these ternary composites containing LCP, the morphology of the dispersed LCP-phase has strong influence on the flow behavior of the composite. Now, concern is how to reach the conditions for the formation of highly elongated LCP domains, i.e. LCP fibrillation, observed in solidified materials. These conditions were investigated for different polymers loaded with fillers of various shapes at micro- and nanometer scales.

The study on multi-scale effect of LCP fibrillation showed that the LCP fibrillation was promoted by the filler addition, depending on the thermodynamic and hydrodynamic driving forces involved.

Premphet and his coworkers[13] have reported that in filled blends the filler distributes selectively in the polymer phase having lowest interfacial tension. Glass beads migrated thermodynamically driven

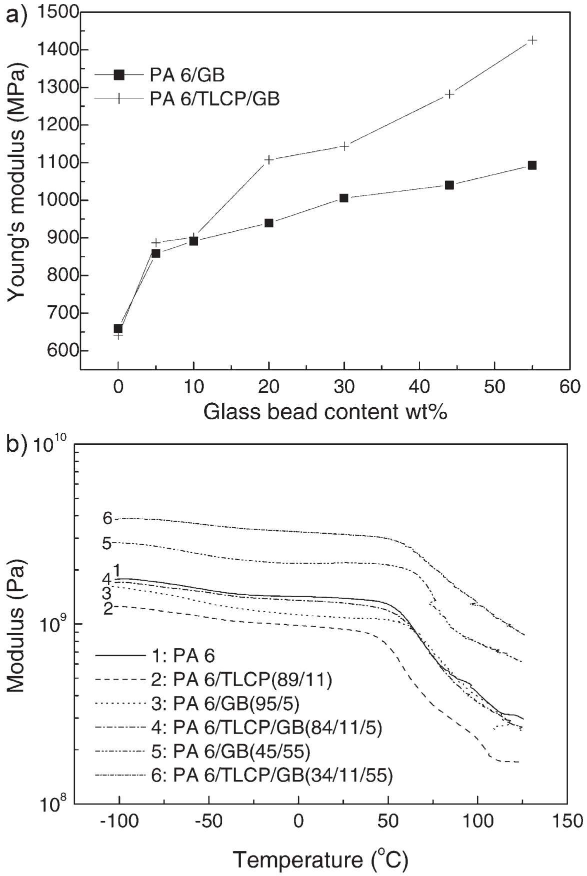

Figure 6.

Young's modulus as a function of glass bead content (a), and dynamic modulus (b) of binary PA6/GB composites and ternary PA6/TLCP/GB composites.[12]

into the vicinity of LCP droplets (Table 1), and thereafter give rise to the hydrodynamic forces that deform the LCP melt droplets.

The influence of hydrodynamic driving forces on the LCP fibrillation can be much clearly understood from the ternary composites filled with glass beads, because of a special feature. After the addition of glass beads, LCP domains in PA6/GB/LCP have curved tails, which definitely resulted from the rolling of glass beads. The rolling effect was so strong that LCP microfibrils having diameters at the order of magnitude of 10 nm were pulled out from the circumference of a melt droplet of LCP, and twisted into a fibril of 1 μm thick by strong local shearing and extensional action (Figure 7).[12]

The in-situ fibrillation of LCP in the PC/LCP melt during shear flow was promoted by the addition of various contents of GB spheres.[14] Increasing the apparent shear rate also facilitated the deformation and fibrillation of LCP as a result of the decreased viscosity ratio (p) and increased capillary number (Ca) at higher shear rates. From the estimation, rheological results showed that neither p nor Ca varied significantly with the addition of GB. But actually the enhancement of LCP fibrillation by adding GB spheres was much more significant than only by increasing the apparent shear rate. It was the hydrodynamic effect of GB spheres that produced the effectively enhanced fibrillation of LCP during processing. When GB spheres were added to the PC/LCP blend and subjected to the externally applied apparent shear, they rotated along the shear direction with a high local shear between the closely neighboring spheres. This high local shear increased the capillary number effectively and promoted the deformation of LCP even at lower apparent shear rates. Moreover, the presence of rotating GB spheres promoted the coalescence of LCP droplets, which also facilitated the deformation and fibrillation of LCP.

Table 1.
Interfacial tension between possible pairs in ternary composites.

Possible pair	Interfacial tension mN/m
PA6-LCP	3.96
PA6-GB	142.6
LCP-GB	125.7
PC-GB	134.1
LCP-GB	115.2

Investigation of the effect of glass bead packing on the LCP fibrillation in PC was conducted with GB of diameter at 2, 5, 20 μm; GB content at 5, 20, 30% (v/v); and shear rate at 20, 1260 s^{-1}.[15] The results revealed two kinds of hydrodynamic effects of GB promoting the LCP fibrillation: at

Figure 7.
Locally magnified morphology of a PA6/GB/LCP 34/55/11 (by wt%) ternary composite at the shear rate of 115.2 s^{-1}.[12]

lower GB packing, the shear flow was enhanced in quantity by the high local shear between glass beads; and for a high enough GB packing, the shear flow was changed in quality to an elongational flow which was more effective for the LCP fibrillation. By adding high amounts of glass beads to LCP/PC blends capillary flow forms very long and highly oriented fibrils of LCP in situ formed.[16] Thermodynamic causes the different interfacial tension between the components make GB migrate to the LCP phase. The different interfacial tensions force the GBs to migrate to the LCP-phase where they create confining conditions (microcapillaries) when high enough in amount. The LCP droplets passing through these microcapillaries under extensional flow form finally stabilizing fibrils.

In the case of PC/nano-silica/LCP, the esterification between PC and LCP molecules during melt blending was significantly reduced in nano-SiO_2 filled LCP/PC blends, compared to the unfilled LCP/PC one.[17] Well-developed LCP fibrils were formed by capillary flow in nano-SiO_2 filled blends. By increasing the nano-SiO_2 concentration and shear rate, the fibrillation of LCP was significantly enhanced.

In ternary composites consisting of an LCP, nano-SiO_2 and polysulfone (PSF),[18] very long and perfectly oriented LCP fibrils were in situ formed in capillary flows by the addition of 5vol% nano-SiO_2. Dynamic rheological analysis indicated that the sharp increase of elasticity was caused by higher content of nano-SiO_2. Then the steady shear rheological measurement and corresponding analyses showed the entrance angle at the entrance of capillary die was decreased and elongational stress increased when the polymer melt flowed through the abrupt contraction, which resulted in LCP fibrillation in PSF/nano-SiO_2/LCP system.

For organophilic montmorillonite (OMMT) filled PA6 in the presence of an LCP, enhanced fibrillation of LCP droplets was attributed to the role of nano-clay particles as a compatibilizer to improve the interfacial adhesion and to suppress the interfacial slip between LCP and polyamide phases in the melt, so that the shear stress was effectively transferred to the dispersed LCP phase.[19]

Through choosing $CaCO_3$ whisker as the filler and polysulfone (PSF) as the matrix, the morphological evolution of LCP droplets has been investigated.[20] In contrast to the spherical or ellipsoidal droplets of LCP formed in binary PSF/LCP blends, the LCP fibrillation was promoted by the introduction of whisker particles in all ternary blends at all applied shear rates. Further analysis of flow field indicated that the predominant factors promoting the LCP fibrillation were the vortex enhanced and elongational stress increased by the whisker in the converging flow area at the entrance of capillary, rather than the viscosity ratio and capillary number. The further analysis of flow field and elasticity of system showed that the addition of longer whisker increased the elastic modulus of material melts more efficiently and enhanced the vortex in the converging flow area at the entry of capillary, which resulted in the increase of the elongational stress and promoted the formation of longer LCP fibrils in PSF/whisker system.[21]

For a clear view, all the results of the multi-scale effect of LCP fibrillation are summarized in Table 2. Except for the above-discussed factors, the geometrical factor in these multi-phase systems also had its influence. It included the size of temporarily formed capillaries in fiber-filled melts[8,9] and the size of gaps between nearby rotating spheres.[14,15] It was the prerequisite for the hydrodynamic driving force to act.

Conclusion

The rheological hybrid effect has been found in multi-component and multi-phase polymer systems containing thermotropic liquid crystalline polymer as the minor phase. It is influenced by several factors, which are briefly described and discussed in this review. It occurs for different combinations of the three ingredients to some extent, different in quality and quantity.

Table 2.
Thermodynamic and hydrodynamic driving forces promoting LCP fibrillation in filled polymer melts.

Matrix	Filler	Thermodynamic	Hydrodynamic	Reference
		Filler dispersion	LCP fibrillation	
PA6	GF		High local shear Elongational flow	[8,9]
PA6	GB	Near LCP	High local shear	[12]
PC	GB	Near LCP	High local shear Elongational flow	[14–16]
PC	Nano SiO_2	PC/LCP	LCP coalescence	[17]
PSF	Nano SiO_2	PSF	Increased elasticity Enhanced vortex	[18]
PA6	OMMT	PA6	Improved interfacial adhesion	[19]
PSF	Whisker	PSF	Enhanced vortex	[20,21]

The multi-scale effect of LCP fibrillation is jointly controlled by thermodynamic and hydrodynamic driving forces together with geometrical factors, so that highly elongated LCP domains are formed with smaller or higher aspect ratio of the LCP fibrils depending on the conditions. The investigation on these features is just at its early stage, the field for deeper understanding and future extension is quite large. Further studies to optimize these effects are needed for tailored practical application.

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