

# A Gradient Structure Formed in Injection-Molded Polycarbonate *In Situ* Hybrid Composites and Its Corresponding Performances

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**ABSTRACT:** Three polycarbonate (PC) composites that were reinforced, respectively, with liquid crystalline polymer (LCP), glass fibers, and both of them were prepared by a single injection-molding process. The role of LCP in improving the processibility of the composites was characterized by torque measurement test. The transitions of LCP morphology in two- and three-component composites were investigated by using polarizing optical microscopy and scanning electron microscopy. The micrographs showed a skin-core gradient structure in all three systems investigated, and the addition of glass fiber to the PC/LCP blend affected the morphological transition and content distribu-

tion of dispersed LCP phase through the thickness of the injection-molded samples. These results were correlated well with the measurements of tensile mechanical properties and dynamic mechanical analysis. How to fully use the dispersed LCP phase in PC *in situ* hybrid composites was discussed for the thickness change of core layer and the heterogeneous distribution of more LCP in the core. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 625–634, 2004

**Key words:** polycarbonates; liquid crystalline polymers (LCP); injection-molding; hybrid; glass fiber; skin-core; DMA

## INTRODUCTION

Many studies of liquid crystalline polymer (LCP) blends have been carried out since the introduction of the concept of *in situ* composites.<sup>1</sup> Most of the studies of LCP blends deal with the morphology evolution of the LCP dispersed phase,<sup>2–4</sup> the miscibility,<sup>5,6</sup> and the compatibility between LCP and the matrix,<sup>3,7–12</sup> as well as the final mechanical properties of the composites.<sup>7,13–16</sup> The low viscosity of the LCPs can reduce the overall viscosity of the blend, with consequent improvement of processibility.<sup>17–19</sup> On the other hand, the LCP fibrils generated *in situ* under proper processing conditions have outstanding reinforcing effect.<sup>20,21</sup> However, the use of common processing methods, such as injection molding, cannot fulfill the roles of LCPs as reinforcing agents, because LCP fibrils formed in such ways have lower mechanical properties than the fibers and strands spun from the same polymer. It is one of the significant limitations of *in situ* composites.<sup>22</sup>

By combining the concept of the *in situ* composite and the advantages of reinforcing effect of macro-

scopic fibers, a concept of *in situ* hybrid composites was put forward by He and coworkers.<sup>23–24</sup> In an *in situ* hybrid composite, the macroscopic fibers act as the main load-bearing agent. They contribute to the large increase of the strength and modulus of the resultant material. The introduction of LCPs aims to decrease the viscosity of the whole blend system. By using the technique of *in situ* hybrid reinforcing, a reinforced material with balanced mechanical and processibility can be obtained.

In hybrid composites, the addition of glass fibers has a great effect on the morphology of LCPs; thus, it also influences the flowability of hybrid composites.<sup>25,26</sup> It is interesting to find that the LCP fibrillation is enhanced by the introduction of glass fibers in a system with Nylon 6 as thermoplastic matrix, although it is well known that LCPs seldom form fibrils in Nylon 6 because of its relatively low melt viscosity. At the same time, the flowability of the hybrid system is greatly improved with the existence of LCP fibrils.<sup>26</sup>

Hu et al.<sup>27</sup> also found a hybrid effect in polypropylene (PP)/LCP/nano-SiO<sub>2</sub> hybrid composites. The formation of LCP fibrils was enhanced with the introduction of nano-SiO<sub>2</sub> fillers into PP/LCP blends. The presence of LCP fibrils improved the flow properties of the PP/LCP/SiO<sub>2</sub> composites. Their further research found that the mixing sequence, the filler size, and the filler surface nature were the main impact

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factors on the morphology of the LCP phase and the rheology of the hybrid composites.<sup>28</sup>

The aim of this study was to investigate the fine structure of PC *in situ* hybrid composites formed during the injection-molding process. A polycarbonate (PC) composite that was reinforced with both glass fiber and LCP was obtained by a single injection-molding process. Two-component composites were also obtained by direct injection molding for comparison. Torque measurements on the composites were employed to characterize the LCP addition with relation to the viscosity reduction in these systems, although in this article we mainly focus on the skin-core gradient structure formed during processing. Optical microscopy and scanning electron microscopy (SEM) investigations were used to reveal the skin-core gradient structure of the composites and elucidate the formation of structure affected by the addition of glass fiber. Tensile mechanical and dynamic mechanical tests were used to compare the mechanical difference between the skin and core layers in the composites. The relationship between the mechanical difference of two layers and the morphological and quantitative differences of reinforcement phase was discussed.

## EXPERIMENTAL

### Materials

The matrix polymer PC, T1260, with  $\bar{M}_w = 26,000 \pm 1000$ , was supplied by Shanghai Zhonglian Chemical Plant (Shanghai, China).

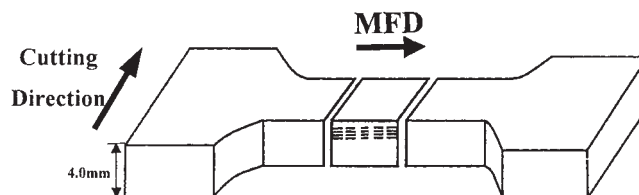
The LCP used in this work was Vectra A950, a wholly aromatic copolyester of 73% hydroxybenzoate (HBA) and 27% hydroxynaphthanoate (HNA) manufactured by Hoechst Celanese, hereafter referred to as VA.

Glass fiber (GF) was a commercial-grade short-cut glass fiber CS 173  $\times$  10C (DSM, the Netherlands) with an initial length of 4 mm and a diameter of 10  $\mu\text{m}$ .

### Sample preparation

The polymers used in this study were dried at 110°C under vacuum for at least 12 h. PC/VA (90/10), PC/GF (80/20), and PC/VA/GF (70/10/20) were dry blended before injection. The dumbbell tensile samples (ASTM D638) were directly injection molded (CJ 150 NC II, Chen Hsong Machinery Co. Ltd., China) without precompounding. The injection temperatures from zone 1 to zone 3 were set at 270, 280, and 285°C. The injection molding was performed with an injection pressure of 7 MPa in a mold kept at 70°C for a complete cycle of 30 s.

The skin and core layers samples (thickness of about 0.8 mm) for tensile test were cut from the tensile



**Figure 1** Schematic representation of cutting location and direction of thin film samples prepared for optical microscope observation.

samples by mechanical method. The unwanted parts were removed by using a cutting saw equipped on a lathe.

The samples for DMA test were cut from the central parallel region of the skin or core layer tensile samples.

### Morphology observation

Thin films,  $\sim 10 \mu\text{m}$  thick, were cut from the central parallel region of the tensile samples by using an ultramicrotome (Leica RM2155, Germany) sequentially from skin to core layers in the transverse direction. The schematic of the cutting direction and location is shown in Figure 1.

To see the shape of the dispersed LCP phase clearly, PC was dissolved away selectively by dropping 1,2-dichloroethane on the thin film. The LCP morphological change from skin to core layers was observed under cross-polarization in an optical microscope (Leica DMLP, Germany).

The fracture surfaces of skin and core layers of the three composites were observed with SEM (Hitachi S-4300, Japan). The fracture surface was obtained by immersing and breaking the skin or core tensile sample in liquid nitrogen and coated with gold.

### Physical and mechanical characterization

#### Blending torque measurements

The processibility of each system was evaluated by recording the torque values during melt processing. The measurement was conducted in a mixer, Haake Rheomix 600, equipped with Haake Rheocod 90 (Karlsruhe, Germany). For each measurement, the material with the same volume was added into the chamber.

#### Tensile measurements

Tensile tests were carried out by using an Instron model 1122 universal testing machine. The strain rate was 1 mm/min for the determination of both tensile strength and elastic modulus. Stress-strain curves for the whole sample and the skin and core layers of the

**TABLE I**  
Steady Torque Values of PC and Its Composites,  
Measured at 280°C

PC : VA : GF	100 : 0 : 0	90 : 10 : 0	80 : 0 : 20	70 : 10 : 20
Torque /N · m	6.1	3.2	8.6	6.5

samples were obtained. The average value of at least five tests was used.

#### Dynamic mechanical analysis

Dynamic mechanical analysis (DMA) was carried out by means of a Perkin–Elmer DMA-7 system from 50 to 200°C. The storage modulus ( $E'$ ), loss modulus ( $E''$ ), and  $\tan \delta$  were measured for the skin and core layer samples. All measurements were conducted in the three-point bending mode at a fixed frequency of 1 Hz and a heating rate of 5°C/min unless otherwise stated.

## RESULTS AND DISCUSSION

### Rheological behavior of the blends in a batch mixer

The torque value of each system was relatively high when the solid materials were introduced into the mixing chamber. Then, it decreased continuously until reaching a steady-state regime with mixing time up to several minutes. The evolution of material with the time in a mixing chamber was just the view of it along the space in an extruder or injector.

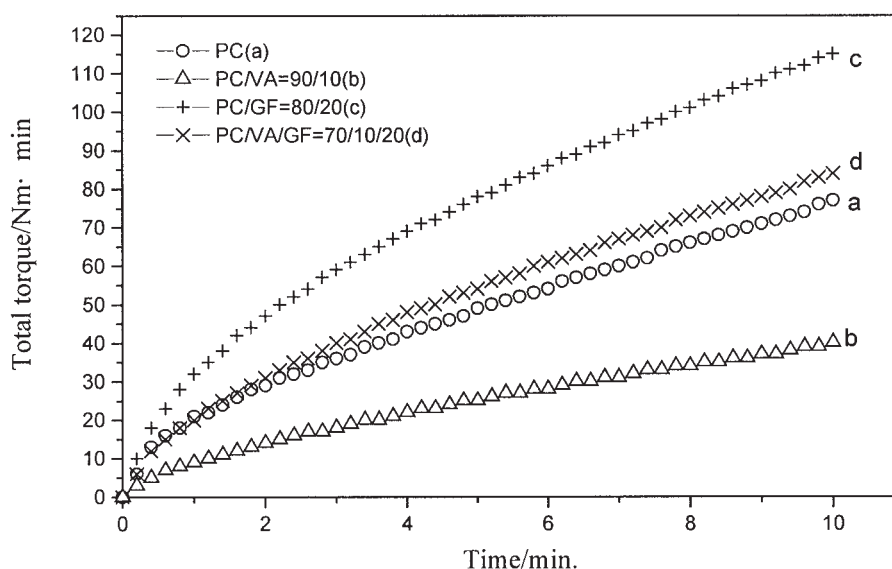
Apparent viscosities ( $\eta_a$ ) have a scaling relationship with the steady torques of the polymer melts when they are processed in a batch mixer at the same rotor

speed and temperature.<sup>29</sup> The steady torque values of the studied systems are listed in Table I. It can be seen that the apparent viscosity of PC matrix increases with 20 wt % GF addition. Content of 10% VA dramatically decreases the viscosities of PC and PC/GF composite. The steady torque value of hybrid composite is decreased to the level of PCs.

As suggested in our previous article, the total torque at a certain time is proportional to the work cost for blending up to a certain time.<sup>24</sup> Because it is the integration value of torque over time, the total torque is a more appropriate parameter to characterize the processibility of polymer composites than the viscosity obtained from a capillary rheometer.

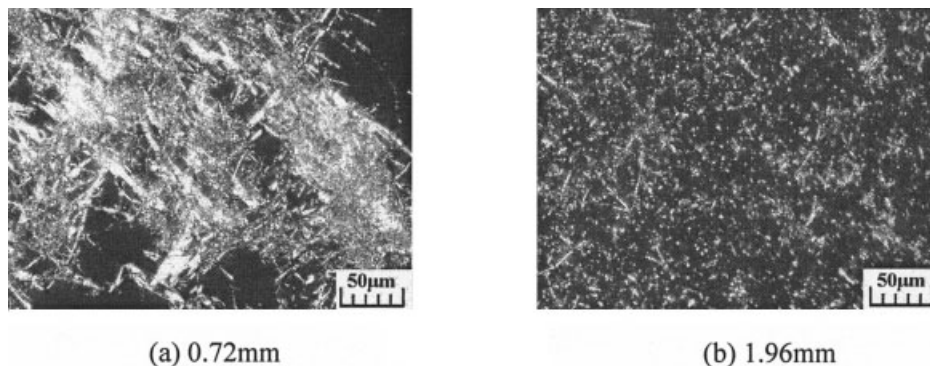
The total torque as a function of blending time for PC, PC/VA, PC/GF, and PC/VA/GF blended at 280°C is shown in Figure 2. It can be seen that the blends with VA addition have a total torque much lower than the corresponding ones. After adding 10 wt % VA, the total torque at 10 min of PC/GF decreases from the original 115 Nm min to 84 Nm min. Similarly, the total torque value of hybrid composite decreases to the level of PCs.

It can be clearly seen that the addition of 10% LCP can improve the processibility of fiber-reinforced polymer composites. In the *in situ* hybrid system, the main role of LCP is to act as a processing aid, but not a reinforced phase as in the *in situ* composites. So, the common processing methods, such as injection molding, which is difficult to fulfill LCPs' role as a reinforcing agent, can be used to process *in situ* hybrid composites. In this study, a single injection-molding step was used to prepare the *in situ* hybrid composite. Its applicability can be concluded from the morphologi-



**Figure 2** Total torque of the PC and its blends as a function of time, mixed at 280°C in Haake Rheomix 600.





**Figure 3** Optical micrographs of LCP phase extracted from PC/VA thin films at different depths from the surface of the 4-mm-thick tensile samples.

cal and mechanical investigation discussed in later sections.

#### A gradient structure shown by morphology observation

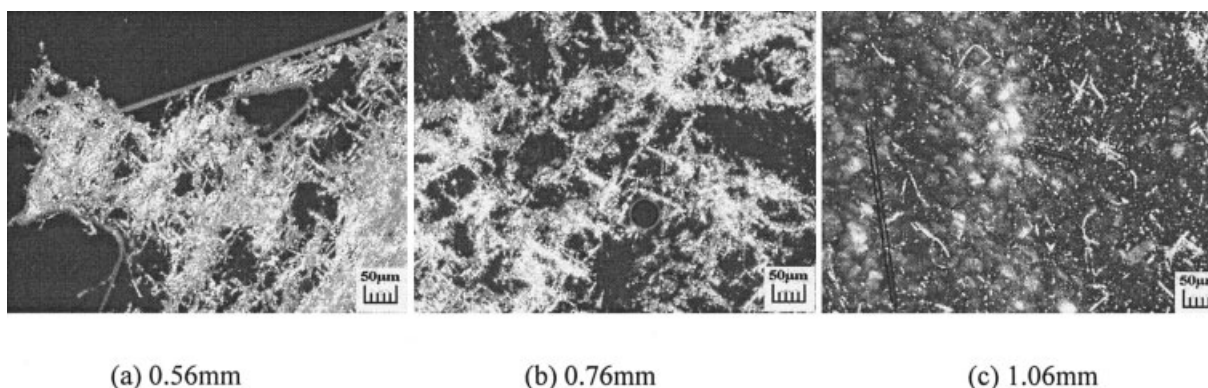
Skin-core structures are commonly investigated not only in LCP/thermoplastics blends<sup>30–32</sup> but also in injected fiber-filled thermoplastic composites.<sup>33</sup> The skin-core gradient structure in these composites can be explained on the basis of flow model given by Tadmor.<sup>34</sup>

The morphological evolution of LCP phase in PC/VA (90/10) observed with an optical microscope is shown in Figure 3. The numbers in the unit of mm in the figure are the depth of the investigated thin films from the surface of tensile sample (ca. 4.0 mm for whole sample thickness). As shown in Figure 3(a), dispersed LCP phase is mainly in the form of fibrils and lamellae in the skin layer. That can also be seen in SEM micrographs, which will be shown later. In this system, the region containing LCP phase in the form of fibrils has a thickness of  $\sim 1.0$  mm. The core region has a thickness only of  $\sim 0.1$ – $0.2$  mm. A sharp bound-

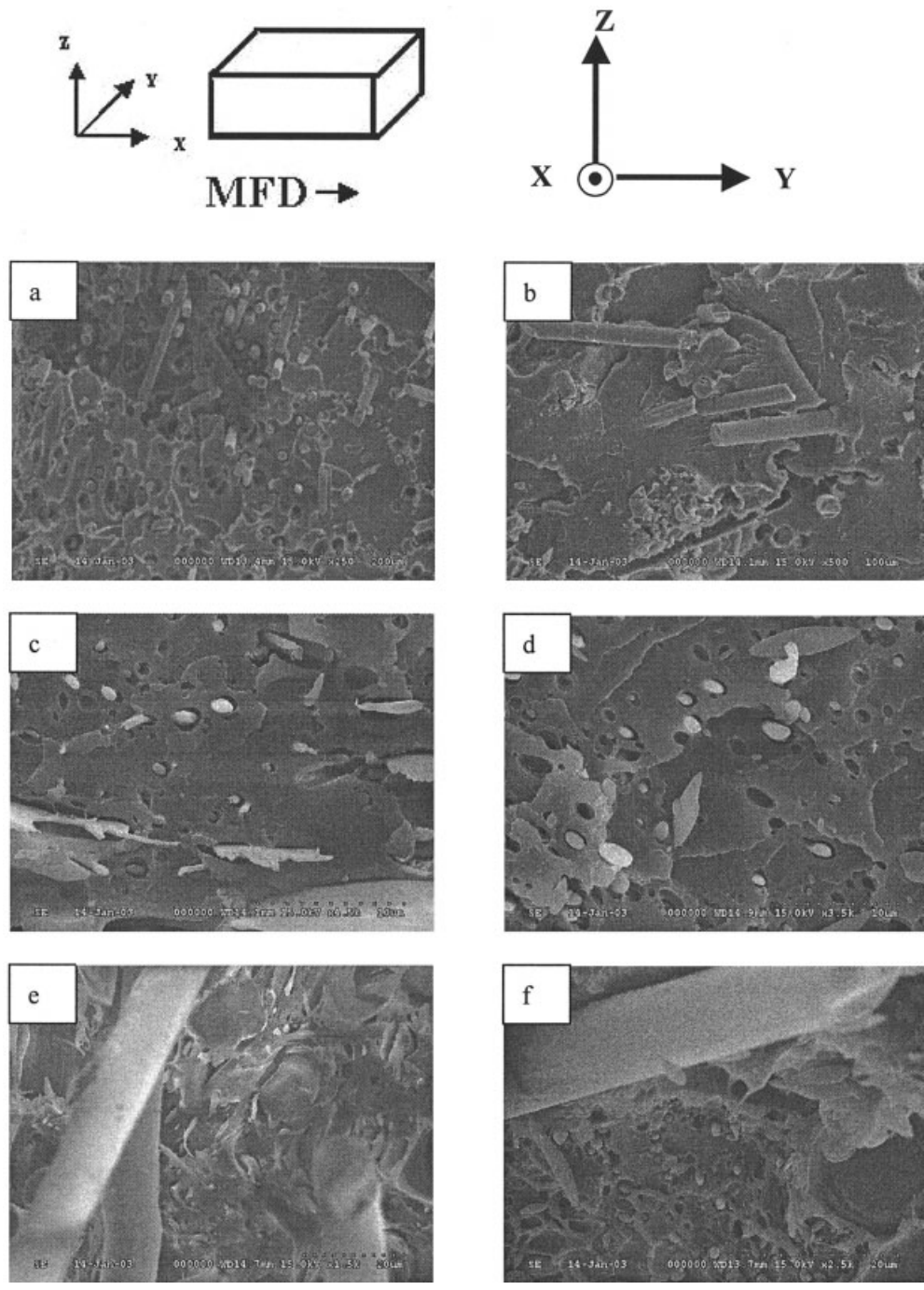
ary between the skin and core layers is difficult to define because of the gradual morphological transition.<sup>35</sup>

The morphology of LCP phase in PC/VA/GF (70/10/20) is shown in Figure 4. Similarly, the numbers in the unit of mm in the figure are the depth of the investigated thin films from the surface of tensile sample. In the skin region, LCP is also in the form of fibrils [Fig. 4(a)]. The skin region has a thickness  $< 0.6$  mm. It is shown in Figure 4(b) that LCP fibrils and microdroplets can all be found in the region at a position (e.g.,  $\sim 0.7$  mm from the surface of tensile bar) that belongs to skin area in PC/VA (90/10) two-component system. The core region has a thickness of  $\sim 2.0$  mm determined by basing on the LCP droplets morphology as shown in Figure 4(c). From these results, it can be said that the addition of glass fibers to the PC/VA *in situ* composite makes the boundary between the skin and core layer shift to the outer region, and the thickness of each layer has marked change.

The SEM micrographs of the fracture surface of skin and core parts for the composites are shown, respectively, in the left and right row in Figure 5. The sur-



**Figure 4** Optical micrographs of LCP phase extracted from PC/VA/GF thin films at different depths from the surface of the 4-mm-thick tensile samples.

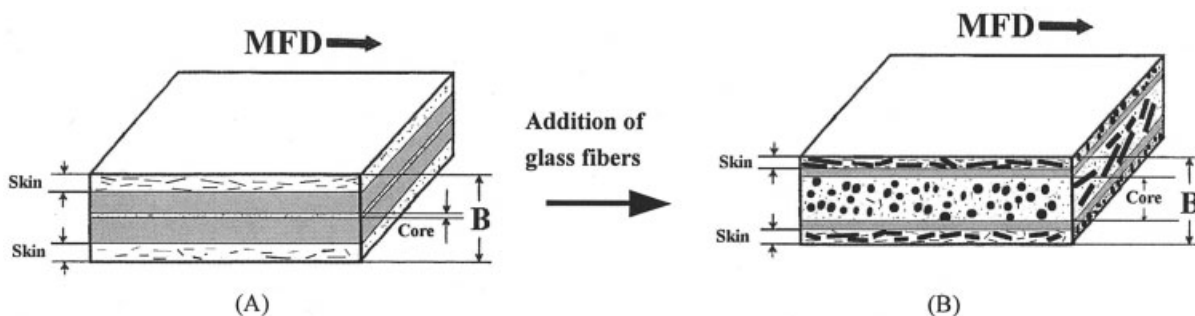


**Figure 5** SEM micrographs of the fracture surfaces of skin (left) and core (right) regions for PC/GF (a, b), PC/VA (c, d), and PC/VA/GF (e, f) composites. The *x*- and *y*-axes in the figure correspond to parallel and perpendicular direction to the MFD. All the investigated surfaces are in *Y-Z* plane perpendicular to MFD.

faces were fractured perpendicular to mold-filling direction (MFD) in liquid nitrogen. A detailed description of the investigated surface with relation to the MFD can be found in the figure. It should be pointed out that some samples were tilted for uncertain degrees for the convenience of investigation.

It can be seen from Figure 5(a) that there are distinct voids around the glass fibers and many fibers have

been pulled out from the matrix. In the skin layer, the glass fibers lie parallel to the MFD, whereas they are preferentially aligned perpendicular to MFD in the core layer. A groove can be clearly seen in the lower part of Figure 5(b). It is a sign of poor interfacial adhesion between glass fibers and matrix. It also indicates the preferred orientation of glass fibers in the core layers.



**Figure 6** Schematic illustration showing the gradient structure basing on morphological investigation: (A) PC/VA and (B) PC/VA/GF hybrid composites. (■) morphological transition area.

In the PC/VA (90/10) blend shown in Figure 5(c, d), the situations are almost the same as what is seen in the optical micrographs (Fig. 3). The skin layer contains fibrils and lamellae of LCP embedded in the PC matrix. In the core region [Fig. 5(d)], the LCP dispersed phase is mainly in the form of particles. In Figure 5(c, d), the holes and cavities can be clearly seen because of the pulling out of LCP phase during the fracture of the samples. It indicates poor interfacial adhesion between LCP and PC matrix for their poor miscibility.

The fracture surfaces of skin and core layers for PC *in situ* hybrid composite (PC/VA/GF 70/10/20) are depicted in Figure 5(e, f). In the skin region, as shown in Figure 5(e), the LCP forms the microfibrils with diameters  $< 2 \mu\text{m}$ , whereas the LCP lamellae that exist in Figure 5(c) have disappeared. Figure 5(f) is almost the additional outcome of figure 5(b, d): glass fibers are preferentially aligned perpendicular to MFD, and LCP phase is mainly in the form of particles.

Combining the micrograph of optical microscopy and SEM observation, it can be said that when the glass fibers are introduced into PC *in situ* composites, they have marked influences on the skin–core gradient structure of PC/VA two-component system: (1) the thickness of skin and core regions are altered, based on the morphology transition of LCP phase; (2) the LCP morphology in the skin layers is influenced by the addition of macrofibers (e.g., the lamella morphology that exists in binary blend disappeared after the introduction of glass fibers). The transition of LCP from lamella to fibril morphology in skin layer also means a better dispersion of LCP phase in hybrid than binary system during the injection process. It is well known that the lamellae is the primitive morphology of minor phase in immiscible polymer blends during blending process. The good dispersion effect may originate from increased local viscosity in the interfacial region with the addition of glass fibers.

Based on the morphological observation, a schematic illustration showing the gradient structures of binary and hybrid composites is shown in Figure 6.

The addition of glass fibers also influenced the LCP content distributions in skin and core layers. It will be shown in the next section.

#### Composition distribution in the gradient structure

In the previous section, the skin–core gradient structure existing in the injected-forming PC composites was clearly shown by morphological investigations. It could be seen that the dispersed LCP phase had distinctly different morphology in skin and core layers. It is a possible reason that can cause mechanical differences between skin and core parts in *in situ* and hybrid PC composites. The second possible reason for mechanical differences in the hybrid composite is the different preferred orientation of GFs in skin and core parts shown in the above section. In this section, the content of reinforcement phase in each layer was determined to show whether it is also a reason that accounts for the mechanical differences. To our knowledge, there is no report on whether the introduction of LCP can cause the heterogeneous distribution of reinforcement in each layer in reinforced composites.

To get the amount of glass fiber in two layers for the composites containing GFs, small parts of the skin and core layer samples after tensile test were calcined. The results showed that the glass fiber contents were almost the same, and differences between the two regions were negligible (18.2 versus 18.5% for PC/GF 80/20; 21.7 versus 21.2% for PC/VA/GF 70/10/20).

A Soxhlet apparatus with 1,2-dichloroethane as a selective solvent was used to remove the PC matrix and therefore the amount of reinforced phase (LCP and GF) was obtained. Thus, the LCP content in PC/VA blend can be obtained directly. By subtracting the GF weight percentage obtained in the above step, the LCP content in PC/VA/GF system can be calculated.

In the PC/VA (90/10) blend, the LCP content in the skin layer was about 11.3 wt %, and that in core layer was about 6.7 wt %. Other authors also found the



**TABLE II**  
The Skin-Core Structure in the Thickness and Composition in PC/VA and PC/VA/GF Composites

System	PC/VA (90/10)		PC/VA/GF (70/10/20)	
	Skin	Core	Skin	Core
Thickness (mm)	1.0	0.1–0.2	0.6	2.0
Content of GF (weight %)	—	—	21.7	21.2
Content of LCP (weight %)	11.3	6.7	8.8	14.2

similar heterogeneous distribution of LCP in PPS/LCP blends.<sup>36</sup> They attributed this phenomenon to the high shear flow near the cavity wall (i.e., skin region) and the component with low viscosity has the tendency to congregate in this region. However, the situation was different in PC/VA/GF (70/10/20) hybrid composite. In this system, the LCP content in the skin layer was less than that in core layer (8.8 wt % for skin layer and 14.2 wt % for core layer). Repeated measurements proved the reproducibility of the result. However, at present it is difficult to give a reasonable explanation on such a LCP distribution.

Based on the results mentioned above, the skin-core structure in the thickness and composition in PC/VA and PC/VA/GF composites is summarized in Table II. The two following points should be remarked to summarize this section: (1) The introduction of LCP had no effect on the content distribution of reinforcement (e.g., glass fibers) in this study. (2) There was heterogeneous distribution of LCP in *in situ* and hybrid composites, but two systems exhibited the opposite manner. There was more LCP in the skin layer of PC/VA composite, whereas there was more in the core of hybrid composite.

### Mechanical properties of parts in the gradient structure

Table III lists the results of the tensile tests [i.e., tensile strength ( $\sigma$ ), elongation at break ( $\epsilon$ ), and tensile modulus ( $E$ )] for the original whole samples, as well as skin and core layer.

As for all three systems, it can be seen that (1) PC/VA/GF hybrid composite has higher tensile strength and modulus than the corresponding two-component composites, PC/VA and PC/GF. The tensile strength of the hybrid composite is 26% higher than that of PC/GF composite with only 10% LCP addition. Therefore, the hybrid system had not only better processibility but also better mechanical properties. (2) The skin layer samples have the highest values for tensile strength and modulus, whereas the core parts have the lowest ones. The tensile strengths of skin parts for PC/VA, PC/GF, and PC/VA/GF composites are 31, 24, and 67% higher than that of corresponding core parts. The modulus differences are 71, 27, and 16%, respectively, for the three composites. The second point also indicated that the skin-core layer structures exist in all three composites as we showed above. (3) The elongations at break ( $\epsilon$ ) of core samples are generally higher than those of skin samples. Moreover, the  $\epsilon$  for the wholes are close to those of skins'. This is probably due to the higher tensile strengths of skin samples than those of cores. The whole samples were more likely to fracture at  $\epsilon$  close to skins samples' while not the core ones, although the core layers had better ductility than the skins.

In addition to above points, it should be noted that nine groups of samples are all fractured in a brittle manner except the core parts of PC/VA binary blend. It can be seen from the stress-strain curves (not shown here) recorded during mechanical measurements. This can be explained by the SEM results. As shown in Figure 5(d), the VA dispersed phase is mainly in the form of particles. At the tensile test temperature, the core parts of binary blends can be considered as a ductile matrix filled with rigid LCP particles. It fractured in the character similar to that of rigid-particle-filled systems. As reported in our previous article,<sup>37</sup> a dispersed LCP phase [a random copolyester of HBA and poly (ethylene terephthalate)] was mainly in the form of spherical droplets in the PC composites. This kind of composite exhibited a yield point and some plastic deformation before final fracture, especially when the interphase between the two components was improved by the addition of a proper amount of compatibilizer.

**TABLE III**  
Tensile Properties of PC Composites

	Whole			Skin			Core		
	$\sigma$ (MPa)	$E$ (GPa)	$\epsilon$ (%)	$\sigma$ (MPa)	$E$ (GPa)	$\epsilon$ (%)	$\sigma$ (MPa)	$E$ (GPa)	$\epsilon$ (%)
PC/VA (90/10)	68.8 ± 4.2	1.8 ± 0.2	5.5 ± 1.1	75.0 ± 3.3	2.4 ± 0.2	4.2 ± 0.6	57.1 ± 1.2	1.4 ± 0.2	19.7 ± 7.4
PC/GF (80/20)	73.2 ± 5.4	3.5 ± 0.2	2.3 ± 0.1	86.5 ± 4.3	3.8 ± 0.3	2.2 ± 0.1	69.7 ± 4.9	3.0 ± 0.4	3.0 ± 0.4
PC/VA/GF (70/10/20)	92.2 ± 7.8	3.8 ± 0.3	2.8 ± 0.3	101.9 ± 1.9	4.2 ± 0.1	2.2 ± 0.4	60.9 ± 8.4	3.6 ± 0.1	1.9 ± 0.2

The tensile behavior for the core layer of PC/VA/GF hybrid composite exceeded our expectations. It had not only the lowest tensile strength but also the lowest strain to failure. Although the LCP content in the core layer of hybrid composite was higher than that in PC/VA composites, the tensile strength and ductility were not improved. A reasonable explanation is the poor interfacial adhesion between the dispersed VA phase and PC matrix. It is comprehensible that the mechanical properties for the blends of two immiscible polymers become worse with the increment of one component. When the LCP content was relatively low, its particles had a positive effect on the toughness of PC matrix. For the core samples of hybrid composite, although the tensile modulus had some improvement relative to PC/GF system, the tensile strength and strain to failure became worse because of the increasing of immiscible LCP phase. The poor interphase adhesion between the dispersed components and matrix hindered the full use of the LCP phase in hybrid composites, although the thickness change of core layer and the heterogeneous distribution of more LCP in the core benefitted from on the toughness improvement of the systems. This is a problem we must solve in our future studies.

By and large, the results of measurements on tensile mechanical properties were correlated well with the skin–core gradient structure that was illustrated by using morphological investigation. The mechanical difference between skin and core layer mainly originated from the different glass fiber orientation, as well as the different LCP morphology and content in the two layers.

### Dynamic mechanical analysis on layer structure

Dynamic mechanical analysis tests were widely used to investigate the phase structure and viscoelastic properties of the polymer blends and composites. It had especially been used to study the layer structure in injected samples.<sup>38</sup> In this work, it was employed to study the physical modification of the PC matrix by the introduction of the reinforcement phase.

Figure 7 shows the dynamic modulus and  $\tan \delta$  values as a function of temperature of each skin and core layers for the three composites in our studies. The  $x$ - and  $y$ -axes in the figure are fixed at the same range for conveniently valuing the differences between three systems. It can be clearly seen that the hybrid system had the highest dynamic modulus. The dynamic moduli vary at the same order as obtained from tensile mechanical test: PC/VA/GF > PC/GF > PC/VA.

For PC/VA composite, as shown in Figure 7(a), the difference between the skin and core parts is not so large because the relatively small amount of LCP addition. The  $\tan \delta$  peak of the skin is lower than that of the core, however. It indicates that in skin layer the restriction on the movement of PC molecules is more

than in the core. The more evident reinforcing effect in the skin layer originated from the fibril morphology and high content of LCP phase in this layer.

For the PC/GF composite, the modulus difference is large in the investigated temperature range and can be clearly seen from curves shown in Figure 7(b). The  $\tan \delta$  peak of the layer sample is also lower than that of the core, which indicates the difference of reinforcing efficiency of glass fibers between two parts. The dynamic mechanical difference in skin and core layers is correlated well with the morphology disparity in the two regions.

As shown in Figure 7(c), the modulus difference between the skin and core layers is largest for PC/GF/VA *in situ* hybrid composites. Examination of the  $\tan \delta$  curve of skin layer for the hybrid composites reveals that a second peak has appeared at higher temperatures than the matrix  $T_g$  (157°C from DMA for pure PC). The  $\tan \delta$  peak of core layer is single but becomes broader and shifts to a higher temperature. This also indicates the existence of the second peak that overlapped with the first one in the  $\tan \delta$  curve of core layer sample.

Two possible reasons put forward for the new peak are (1) the presence around the reinforcement of an interphase region with a higher  $T_g$ <sup>39</sup>; (2) the orientation of matrix molecules that is lost at a temperature higher than  $T_g$ . Point 2 is not reasonable in our study because the second peak does not present in PC/VA and PC/GF composite, although the molecular orientation also exists in these two systems, that can be identified from the investigation by using polarized optical microscopy.

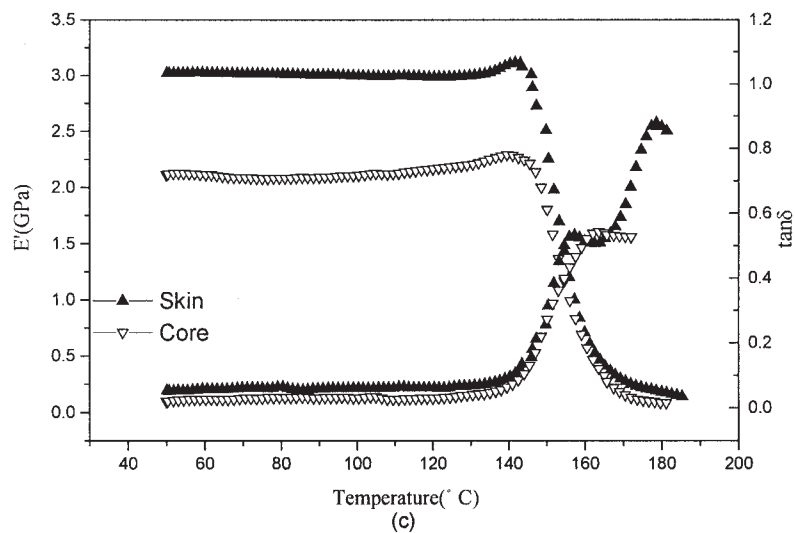
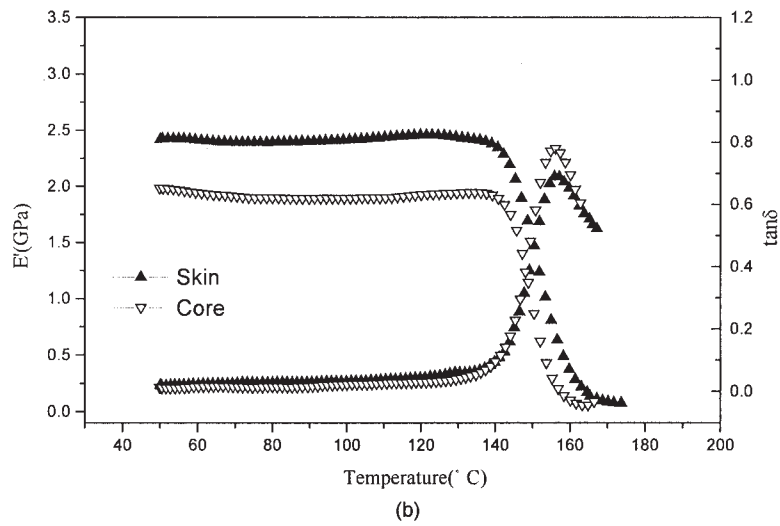
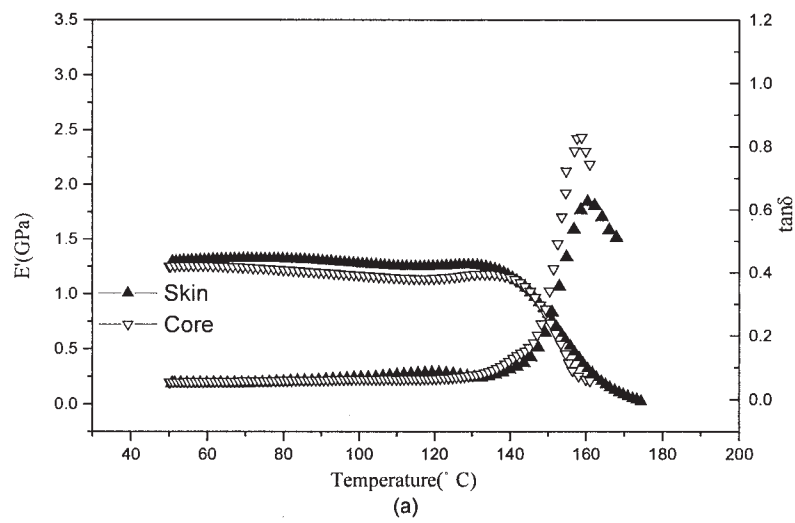
Different hypotheses were suggested for the second peak in the  $\tan \delta$  curve of multicomponent polymeric system. It has been widely accepted that the second peak originates from an interfacial region, although its *in situ* detection and characterization remain difficult.<sup>40</sup> To illustrate how the dynamic mechanical behaviors are affected by the introduction of reinforcements at two different orders of magnitude, as well as the origin of the second peak in damping curves, more studies on *in situ* hybrid composites with compositions different from that in this article are needed.

Paul et al.<sup>41</sup> used the dynamic mechanical analysis to determine HDT of glass fibers reinforced, rubber toughened nylon 6 systems. The same method was used here to investigate the HDT values of skin and core regions in the composites we studied. The results are listed in Table IV.

First, the results show that there are also HDT differences between the skin and core samples. Second, PC/VA/GF hybrid composite has the highest HDT values for both skin and core samples. Clearly, it was also the outcome of the hybrid reinforcing effect of LCP and glass fibers.

HDT differences between two regions at low load (outfiber stress = 0.445 MPa) were relatively large. At





**Figure 7** Dynamic modulus and damping factor ( $\tan \delta$ ) curves for skin and core layer in tensile samples of (a) PC/VA, (b) PC/GF and (c) PC/VA/GF composites PC/VA/GF.

**TABLE IV**  
**Heat Distortion Temperature (HDT) for Skin and Core Layer in Each Composite Determined from DMA Tests**

System	HDT@1.82 MPa	HDT@0.455 MPa
PC/VA		
Skin	147°C	163°C
Core	147°C	159°C
PC/GF		
Skin	154°C	163°C
Core	149°C	156°C
PC/VA/GF		
Skin	158°C	173°C
Core	156°C	167°C

this load, the HDT values of PC/GF are the same or lower than those of PC/VA. This does not conform to the measurement results of tensile moduli for these two systems. It can be said that the HDT at high load (outfiber stress = 1.82 MPa) is more meaningful in discriminating the reinforcing effect of fibers in fiber-filled composites. For this aspect, it could be decided that the reinforcements in *in situ* hybrid composites have more strengthening effect. The mechanical behaviors of hybrid composites are like that of macrofiber-filled composites (e.g., PC/GF system here) more because of the main load-bearing role of macrofibers in *in situ* hybrid composites.

### CONCLUSION

In this study, three PC composites that reinforced, respectively, with LCP, glass fibers, and both of them were prepared by using a single injection process. The skin–core gradient structure in these composites was investigated by using optical microscopy and SEM. It was shown that the addition of glass fibers had great influence on the morphological and content distribution of dispersed LCP phase in hybrid composites. The results of tensile tests and dynamic mechanical analysis correlated very well with the skin–core structure in injected samples. From the results of mechanical and rheological measurement, the conclusion could be made that the *in situ* hybrid composites have good mechanical performance and satisfied processibility.

Based on our previous studies on the PC composites with sphere-dispersed LCP phase,<sup>37</sup> the increment of core layer thickness and the heterogeneous distribution of more LCP in the core should have benefitted from the toughness improvement of hybrid composite if the poor adhesion between the LCP and PC matrix was improved. The addition of an appropriate compatibilizer into the blends containing LCP can achieve this goal and benefit from the toughening effects of dispersed LCP phase.<sup>42,43</sup> The work on this issue has been done and will be reported in the future.

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### References

- Kiss, G. *Polym Eng Sci* 1987, 27, 410.
- He, J. S.; Bu, W. S.; Zhang, H. Z. *Polym Eng Sci* 1995, 35, 1695.
- Seo, Y. S.; Hong, S. M.; Kim, K. U. *Macromolecules* 1997, 30, 2978.
- Seo, Y. *Macromol Symp* 1999, 147, 201.
- Jung, H. C.; Lee, H. S.; Chun, Y. S.; Kim, S. B.; Kim, W. N. *Polym Bull* 1998, 41, 387.
- Lee, H. S.; Jung, H. C.; Han, M. S.; Lee, C. S.; Kim, W. N. *Polymer* 2001, 42, 2177.
- O'Donnel, H. J.; Baird, D. G. *Polymer* 1995, 36, 3113.
- Seo, Y. S. *J Appl Polym Sci* 1998, 70, 1589.
- Vallejo, F. J.; Eguiazabal, J. I.; Nazabal, J. *Polymer* 2000, 41, 6311.
- Garcia M.; Eguiazabal J. I.; Nazabal J. *Polym Compos* 2002, 23, 592.
- Zhang J.; He J. S. *Polymer* 2002, 43, 1437.
- Zheng X. J.; Zhang, J.; He, J. S. *J Appl Polym Sci* 2003, 87, 1452.
- Tjong, S. C.; Meng, Y. Z. *J Appl Polym Sci* 1998, 70, 1611.
- Wong, S. C.; Mai, Y. W.; Leng, Y. *Polym Eng Sci* 1998, 38, 156.
- Tjong, S. C.; Jiang, W. *Polym Compos* 2000, 21, 941.
- Li, Z. G.; Narh, K. A. *Compos Part B-ENG* 2001, 32, 103.
- Isayev, A. I.; Subramanian, P. R. *Polym Eng Sci* 1992, 32, 85.
- Meng, Y. Z.; Tjong, S. C.; Hay, A. S. *Polymer* 1998, 39, 1845.
- Bastida, S.; Eguiazabal, J. I.; Nazabal, J. *J Mater Sci* 2000, 35, 153.
- Sukhadia, A. M.; Datta, A.; Baird, D. G. *Int Polym Proc* 1992, 7, 218.
- Wiff, D. R.; Weinert, R. J. *Polymer* 1998, 39, 5069.
- Baird, D. G.; McLeod, M. A. in *Polymer Blends*; Paul, D. R.; Bucknall, C. B., Eds.; Wiley: New York, Vol. 2, 2000.
- He, J. S.; Zhang, H. Z.; Wang, Y. L. *Polymer* 1997, 38, 4279.
- He, J. S.; Wang, Y. L.; Zhang, H. Z. *Comp Sci Tech* 2000, 60, 1919.
- Zheng, X. J.; Zhang, B. Q.; Zhang, J.; Xue, Y. F.; He, J. S. *Int Polym Proc* 2003, 18, 3.
- Zheng, X. J.; Zhang, J.; He, J. S. *J Polym Sci Part B: Polym Phys* 2004, 42, 1619.
- Lee, M. W.; Hu, X.; Yue, C. Y.; Li, L.; Tam, K. C.; Nakayama, K. *J Appl Polym Sci* 2002, 86, 2070.
- Lee, M. W.; Hu, X.; Li, L.; Yue, C. Y.; Tam, K. C. *Polym Int* 2003, 52, 276.
- Bousmina, M.; Ait-Kadi, A.; Faisant, J. B. J. *Rheol* 1999, 43, 415.
- Blizard, K. G.; Federici, C.; Federici, O.; Chapoy, L. L. *Polym Eng Sci* 1990, 30, 1442.
- Silverstein, M. S.; Hiltner, A.; Baer, E. *J Appl Polym Sci* 1991, 43, 157.
- Mehta, A.; Isayev, A. I. *Polym Eng Sci* 1991, 31, 971.
- Karger-Kocsis, J. in *Polymer Blends*; Paul, D. R.; Bucknall, C. B., Eds.; Wiley: New York, Vol. 2, 2000.
- Tadmor, Z. *J Appl Polym Sci* 1974, 18, 1753.
- Chik, G. L.; Li, R. K. Y.; Choy, C. L. *J Mater Process Tech* 1997, 63, 488.
- Shonaike, G. O.; Hamada, H.; Yamaguchi, S.; Nakamichi, M.; Maekawa Z. *J Appl Polym Sci* 1994, 54, 881.
- Xue, Y. F.; Zhang, J.; Zheng, X. J.; He, J. S. *J Appl Polym Sci* 2003, 89, 1493.
- Jarus, D.; Scheibelhoffer, A.; Hiltner, A.; Baer, E. *J Appl Polym Sci* 1996, 60, 209.
- Tsagaropoulos, G.; Eisenberg, A. *Macromolecules* 1995, 28, 6067.
- Colombini, D.; Maurer F. H. J. *Macromolecules* 2002, 35, 5891.
- Laura, D. M.; Keskkula, H.; Barlow, J. W.; Paul D. R. *Polymer* 2002, 43, 4673.
- Chiou, Y. P.; Chang, D. Y.; Chang, F. C. *Polymer* 1996, 37, 5653.
- Chang, D. Y.; Chang, F. C. *J Appl Polym Sci* 1995, 56, 1015.