

In Situ Composites from Blends of Polycarbonate and a Thermotropic Liquid-Crystalline Polymer: The Influence of the Processing Temperature on the Rheology, Morphology, and Mechanical Properties of Injection-Molded Microcomposites

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ABSTRACT: This work was aimed at understanding how the injection-molding temperature affected the final mechanical properties of *in situ* composite materials based on polycarbonate (PC) reinforced with a liquid-crystalline polymer (LCP). To that end, the LCP was a copolyester, called Vectra A950 (VA), made of 73 mol % 4-hydroxybenzoic acid and 27 mol % 6-hydroxy-2 naphthoic acid. The injection-molded PC/VA composites were produced with loadings of 5, 10, and 20 wt % VA at three different processing barrel temperatures (280, 290, and 300°C). When the composite was processed at barrel temperatures of 280 and 290°C, VA provided reinforcement to PC. The resulting injection-molded structure had a distinct skin-core morphology with unoriented VA in the core. At these barrel temperatures, the viscosity of VA was lower than that of PC. However, when they were processed at 300°C, the VA domains were dispersed mainly in spherical droplets in the PC/VA composites and thus were unable to reinforce the material. The rheological measurements showed that now the viscosity of VA was higher than that of PC at 300°C. This structure development during the injection molding of these composites was manifested in the mechanical properties. The tensile modulus and tensile strength of the PC/VA composites were dependent on the processing temperature and on the VA concentrations. The modulus was maximum in the PC/VA blend with 20 wt %

VA processed at 290°C. The Izod impact strength of the composites tended to markedly decrease with increasing VA content. The magnitude of the loss modulus decreased with increasing VA content at a given processing temperature. This was attributed to the anisotropic reinforcement of VA. Similarly, as the VA content increased, the modulus and thus the reinforcing effect were improved comparatively with the processing temperature increasing from 280 to 290°C; this, however, dropped in the case of composites processed at 300°C, at which the modulus anisotropy was reduced. Dynamic oscillatory shear measurements revealed that the viscoelastic properties, that is, the shear storage modulus and shear loss modulus, improved with decreasing processing temperatures and increasing VA contents in the composites. Also, the viscoelastic melt behavior (shear storage modulus and shear loss modulus) indicated that the addition of VA changed the distribution of the longer relaxation times of PC in the PC/VA composites. Thus, the injection-molding processing temperature played a vital role in optimizing the morphology-dependent mechanical properties of the polymer/LCP composites. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 34–45, 2007

Key words: composites; injection molding; mechanical properties

INTRODUCTION

Blending liquid-crystalline polymers (LCPs) with thermoplastic polymers offers the generation of new engineering materials with relatively low costs and improved properties.^{1–7} These composite materials

combine the compressive strength of the matrix polymer with the tensile strength of the LCP phase. In comparison with composites filled with rigid fibers and fillers, particularly glass and carbon fibers, the most advantageous point of LCP-reinforced composites is that as LCPs form ordered fluids with few entanglements, they facilitate the processing of a polymer by lowering the melt viscosity.^{8,9} The fibril formation of LCPs in LCP-reinforced composites depends on the combination of shear and elongational stresses experienced by the composites during processing^{3–7,10,11} and can be understood through the theory of drop deformation originally developed by Taylor.¹² It has been well observed that an LCP dispersed phase is elongated more effectively in the entrance region by extensional stress^{10,13} than in shear flow.^{11,13}

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Among the various types of processing methods, injection molding is used to prepare polymer blends in industry. However, injection-molded polymer blends usually have low mechanical properties, generally below the values calculated from the rule of mixing, even though in recent years various research groups have reported on the development of a blend morphology for better mechanical performance with injection-molding machines. In this context, it is widely known that in injection-molded LCP/polymer composite materials, a skin-core morphology is observed. The core and skin have a gradient structure and again are subdivided into ordered and disordered layers. This resulting layered morphology is mainly due to the expanding radial flow near the mold gate, known as the fountain flow of the moving melt, and the nonisothermal shear flow into the mold cavity.¹¹ The elongational flow in the injection direction at the cold mold surface yields a highly oriented layer reinforced with elongated LCP, whereas the shear flow at the central core region yields unoriented LCP. In fact, this is a significant drawback of injection-molded *in situ* composites that results in a planar anisotropic distribution of high-flow-directional and low-transverse-directional mechanical properties.^{14,15}

The large aspect ratio of the elongated LCP creates optimum conditions for reinforcement, which is again highly dependent on the processing conditions. Isayev¹⁶ developed a new technique for the injection molding of self-reinforcing polymer/LCP composites, in which the injection-molding temperature is the major parameter to achieve microfibrillar structures of the LCP phase in the polymer matrix. Zulle et al.¹⁷ observed better tensile modulus and strength properties in the flow direction of injection-molded Vectra copolyester at low values of the injection pressure and injection rate, which they correlated to the improved skin-core morphology. Ophir and Ide¹⁸ reported that the mechanical properties of a wholly aromatic LCP copolyester increase with an increasing processing temperature. Similarly, Lekakou et al.¹⁹ optimized the processing conditions for the self-reinforcing behavior of Vectra in a nylon-6,6 matrix and observed that a low injection pressure of 50 MPa and a melting temperature of 300°C led to better modulus and tensile strength. Siegmann et al.⁷ observed a significant improvement in the tensile modulus and strength with a reduction in the elongation for injection-molded polyamide/LCP blend samples.

Berry et al.²⁰ reported on the relationship between the morphology that develops during the injection molding of polyblends containing LCPs and their mechanical properties. They observed that the formation of a fibrillar reinforcing LCP phase and thus enhanced mechanical properties are mainly dependent on the viscosity ratio and the interfacial forces between the two phases in the blends. Isayev and

Modic⁴ studied blends of polycarbonate (PC) and a naphthoic acid based LCP. A fibril morphology was observed only at low (<10 wt %) concentrations of the LCP. At higher concentrations of the LCP, they found a droplet morphology with poor mechanical properties for injection-molded blend samples. However, some improvements in the mechanical properties of injection-molded PC/30 wt % hydroxyl benzoic acid based LCP blend samples was reported by Blizard and Baird.⁵ Similarly, in the case of PC/60 wt % hydroxybenzoic acid based LCP blends, Zhuang et al.²¹ also reported improvements in the tensile properties due to the presence of the LCP phase in a fibril form.

Although only a few of the aforementioned articles, particularly those on injection-molded PC/LCP blends, are reviewed here, no systematic attempt is reported in the literature to identify and correlate the processing conditions for generating an LCP fibril morphology and consequently the improvements in the mechanical properties of these blends. Contrary to this, McLeod and Baird²² and Bafna et al.²³ reported the influence of processing variables on the final mechanical properties of injection-molded poly(ethylene terephthalate)/LCP composites. They observed that the injection-molding barrel temperature, which also governed the flow kinematics during mold filling, had a tremendous effect on the properties of these molded samples. Several operating parameters, such as the mold temperature, injection temperature, injection speed, screw and nozzle temperature, and barrel dwelling time, affect the evolution of the blend morphology during the injection-molding process.^{18,22,26-28} In fact, we have observed in our laboratory²⁹ that in comparison with other operating parameters, the injection-molding processing (barrel) temperature has a dominating effect on the mechanical properties of composites and in fact ultimately governs the physical states of the composite melts. The other parameters have a marginal effect. Despite numerous efforts to identify the various processing factors in injection molding, we still do not have a clear understanding of under what combination of processing parameters a dispersed fibril blend morphology will be formed and in turn affect mechanical property enhancements in self-reinforcing composites. However, during this work, keeping the mold temperature constant, we decided to concentrate on the barrel temperature during blend processing. Also, after several molding experiments, we selected a larger nozzle tip with a 3-mm exit diameter, producing higher elongations to fracture (%).

It was the intent of this study to determine basically how the injection-molding process temperatures affects the final mechanical properties of composite materials based on PC reinforced with a thermoplastic liquid-crystalline polymer [Vectra A950 (VA)]. As

TABLE I
Injection-Molding Processing Parameters for PC and PC/VA Blends

Sample	Temperature (°C)				Injection pressure (MPa)	Injection holding pressure (MPa)	Nozzle-tip diameter (mm)	Residence time in the mold (min)
	Zone 1	Zone 2	Zone 3	Mold				
PC	268	275	280	116	91	10	3	2
	278	285	290	116				
	288	295	300	116				
PC/VA blend	268	275	280	116	46	10	3	2
	278	285	290	116				
	288	295	300	116				

a result, an optimum processing barrel temperature has been determined corresponding to the best self-reinforcing morphology that, in turn, will influence the molecular relaxations and thus finally prevent agglomerations of the VA fibrils. It will then be possible to process these injection-molded composites for better mechanical properties.

EXPERIMENTAL

Materials

PC (Lexan-grade), generously supplied by GE Plastics India, Ltd. (Mumbai, Maharashtra, India) was used as the matrix polymer. It had a glass-transition temperature of 145°C. The LCP used in this study was VA, a wholly aromatic random copolyester made of 73 mol % 4-hydroxybenzoic acid and 27 mol % 2-hydroxy-6-naphthoic acid units, that was produced and generously supplied by Polyplastic (Tokyo, Japan). It was an unfilled grade with all the properties associated with liquid-crystalline polymers. The nematic transition point of the VA granules was observed at 282°C, as measured by differential scanning calorimetry (DSC). Above this temperature, VA formed a nematic melt.

Injection molding

PC exhibits hydrolytic sensitivity at the high temperatures needed for processing; it should be dried to less than 0.02% moisture before being processed on standard equipment. The pellets of both PC and VA were first tray-dried at 100°C in an air-circulating oven for about 10 h. The dried materials were tumbled together in predetermined weight ratios in a container before being molded. The resulting mixture was then passed onto the hopper of the injection-molding machine. The melt blending occurred during the plasticization and conveyance of the polymer within the injection-molding machine. The injection-molding machine used for the process was an Arburg (Knightdale, NC) model 220-90-350 injection-molding machine equipped with a 25-mm-diameter screw, an

insulated nozzle tip, and a check ring nonreturn value. The injection pressure (46 MPa), screw speed (200 rpm), nozzle tip with a 3-mm exit diameter, and mold temperature (116°C) were held constant. The injection-holding pressure was set at about 10 ± 1 MPa. The residence time in the injection mold was about 2 min. All the injection-molded composites were produced with loadings of 5, 10, and 20 wt % VA under processing conditions identical to those mentioned previously, except for the processing temperature, and this was carried out in a single step of injection molding.

The injection-molding runs were carried out at three melting temperatures (280, 290, and 300°C). The zone temperatures were varied according to the material being injected. The processing temperatures of the injection molding are listed in Table I. However, the injection pressure used for molding the blends had to be reduced by half with respect to that of neat PC (91 MPa) to overcome flash problems during mold filling. This indicates the reduction in the PC viscosity in the PC/VA blends. The molds were dog-bone-shaped tensile bars of ASTM Standard 638 and notched Izod impact testing samples of ASTM D 256.

Thermal characterization

The thermodynamic transition temperatures of the matrix polymer PC, VA, and PC/VA blends were measured with a PerkinElmer (Waltham, MA) model 7 differential scanning calorimeter operating on a UNIX platform under a continuous nitrogen flow. Temperature scans from 30 to 300°C at a heating rate of 5°C/min were carried out. The DSC apparatus was calibrated for the melting temperature (156.4°C) and enthalpy of fusion (28.840 J/g or 6.79 cal/g) with an indium standard.

Rheological characterization

Dynamic oscillatory rheological measurements of the PC/VA blends and the pure materials were performed with a Haake RT 20 rheometer (Karlsruhe, Germany) equipped with parallel-plate sensor geom-

etry. The measurements were carried out in a constant-stress mode with a shear rate variation of $0.001\text{--}10,000\text{ s}^{-1}$, with the strain values determined with a stress sweep to lie within the linear viscoelastic region. The samples were injection-molded circular disc samples 60 mm in diameter and 1 mm thick. Before the rheological measurements, the samples were dried in an oven at 100°C for about 10 h to remove the possible moisture content. The samples were put between the two plates of the rheometer with a preadjusted gap of 1.01 mm. The measurements were carried out at three different temperatures of 280, 290, and 300°C , which were the same as the processing barrel temperatures during injection molding. The measurements were begun after temperature stabilization.

Morphology

The morphology of the different samples was examined with a Philips XL 30 (The Netherlands) scanning electron microscope with an accelerating voltage of 10 kV. The scanning electron microscopy (SEM) studies were carried out on the fractured samples of the tensile specimens. The tensile specimens were immersed in liquid nitrogen for at least 5 min and then fractured in the direction normal to the tensile direction. These fractured surfaces subsequently were mounted on stubs and coated with a layer of gold to enhance the conductivity and were then observed by SEM.

Mechanical properties

All the tensile properties were measured with an LR 50K universal testing machine from Lloyd (Fareham, Hants, UK) equipped with a 50-kN cell. Standard tensile tests were carried out according to ASTM D 638 (1996) on injection-molded dog-bone specimens. The test specimens were strips 215 mm long, 19.20 mm wide, and 3.00 mm thick. The crosshead speed was set at 50 mm/min. An extensometer with a gauge length of approximately 50 mm was used to measure the elongation. The reported tensile values were averages of at least five samples.

Notched Izod impact tests were carried out under ambient conditions according to the ASTM D 256 method with a Tinius Olsen (Horsham, PA) model 892 impact testing machine.

The dynamic mechanical properties of the injection-molded specimens were obtained with a dynamic mechanical thermal analyzer. The dynamic mechanical responses of the injection-molded specimens at 280, 290, and 300°C were obtained with a Rheometric Scientific MK-3 model dynamic mechanical analyzer from Polymer Laboratories, Inc. (Mumbai, Maharashtra, India). The data were collected in the single-cantilever mode on a computerized data-acquisi-

tion station. The sinusoidal stress was applied to the samples at a frequency of 1 Hz and a constant strain of X4 (four Times). A heating rate of $2^\circ\text{C}/\text{min}$, with a soaking time of 2 min to establish thermal equilibrium in the range of $30\text{--}200^\circ\text{C}$, was used. Measurements were performed on medium, rectangular-frame samples with a sample geometry of $8.0\text{ mm} \times 8.0\text{ mm} \times 1.5\text{ mm}$.

Fourier transform infrared (FTIR) studies

The possible chemical interactions that could occur between the PC and VA phases in composites during injection molding were investigated with a PerkinElmer 500 Paragon FTIR spectrometer at a resolution of 4 cm^{-1} . The neat PC and 80/20 (wt %/wt %) PC/VA composite materials, injection-molded at 280, 290, and 300°C , were used to prepare thin films. The different thin films were prepared for spectral analysis by the melting of the materials at 280, 290, and 300°C while sandwiched between two microscope glass coverslips.

RESULTS AND DISCUSSION

Compatibility in the PC/VA composites

The DSC thermograms of the PC/VA (Fig. 1) blends reveal two transitions. The first one around 142°C is associated with the glass-transition temperature of a PC-rich phase in the PC/VA blends, whereas the second one, in an endothermic peak appearing at a melting temperature of 282°C , is ascribed to the melting of the crystalline VA phase. Despite the low sensitivity

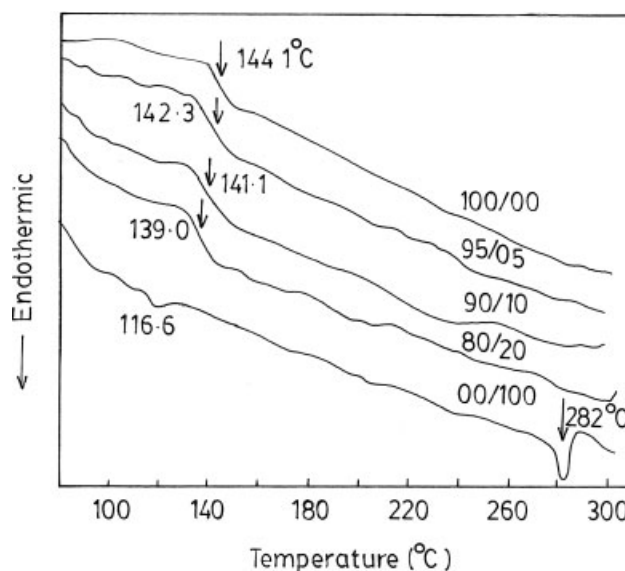


Figure 1 DSC curves for 100/00, 95/05, 90/10, 80/20, and 00/100 (wt %/wt %) PC/VA blends samples injection-molded at 300°C .

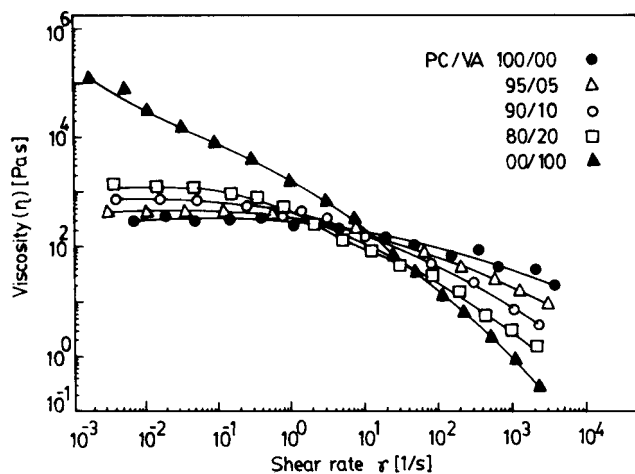


Figure 2 Shear viscosity of the pure components (PC and VA) and their blends (samples injection-molded at 290°C) by parallel-plate rheometry at 280°C.

of the DSC technique, a slight decrease in the glass-transition temperature of PC with increasing VA content in the blends can be observed in the thermographs. This depression in the glass-transition temperature may be due to the plasticizing effect of VA in the blends. To ascertain this observed depression of the glass-transition temperature of the PC matrix in the blends, a dynamic mechanical thermal analysis was also carried out for these blends. A progressive shift of the dynamic tensile loss modulus ($\tan \delta$) of PC to lower temperatures was observed with increasing VA content in the blends, confirming that VA plasticizes the PC matrix. The figures related to these results are presented later. This is also well reflected in the lowering of the blend viscosity. In the case of the blends, possible transesterification reactions may occur between PC and VA during the injection-molding process.^{30–32} However, no reaction could be detected after the processing of the blends. The only infrared absorption peak was observed at 1780 cm^{-1} , similar to that of pure PC and the absence of the typical ester group; the frequencies in this case, at $1730\text{--}1740 \text{ cm}^{-1}$, indicate that amorphous PC does not undergo chemical reactions when blended with crystalline VA at high processing temperatures (280–300°C).

Rheological behavior

The flow curves of the PC, VA, and PC/VA blend system at 280°C are shown in Figure 2. The viscosity data in general cover a range of shear rates from 10 to 10^3 s^{-1} . Pure PC shows Newtonian flow behavior at low shear rates. However, at high shear rates, it exhibits a tendency for shear thinning. In the case of pure VA, the viscosity decreases sharply with increasing shear rates. It also exhibits shear-thinning behavior, particularly at higher shearing rates. However,

the viscosity of VA is higher than that of the pure PC matrix in low and intermediate shear rate ranges, and this reverses at the cross overpoint. At this crossover point, a shear rate of about 20 s^{-1} , the flow curves of the VA and the PC matrix intersect, and when the shear rate is above the crossover point, the viscosity ratio of VA to PC is less than unity. It is commonly observed that maximum fibrillation occurs when the viscosity ratio of an LCP to a polymer matrix is smaller than or near unity.^{4–6,33}

In the case of PC/VA blends, similar flow characteristics have been observed. However, with increasing VA contents in the blends and particularly for a blend with 20% VA, it crosses over the PC flow curve at a low shear rate (0.2 s^{-1}), exhibiting Newtonian behavior in this shear region, followed by continuous shear thinning. Also, at higher shear rates ($>20 \text{ s}^{-1}$), the viscosity drop is faster with increasing VA content, even though the viscosities of the blends are still intermediate between those of the neat PC and VA components at higher shear rates.

Figure 3 shows the viscosity curves measured for the PC, VA, and PC/VA blend system at 290°C. A similar rheological nature can be observed also at 290°C. The only difference is that the shear thinning at 290°C is observed at lower shear rates (ca. 10 s^{-1}) than that at 280°C. Also, the crossover point for the flow curves of PC and VA is shifted toward a much lower shear rate of about 0.2 s^{-1} .

The viscosity values of the neat PC, VA, and PC/VA blends at 300°C (Fig. 4) show anomalous behavior. At low shear rates (ca. 0.1 s^{-1}), the blends and the pure PC exhibit Newtonian behavior, but there is a marked increase in the viscosity of the blends compared with that of pure PC. At higher shear rates ($>0.1 \text{ s}^{-1}$), although shear thinning in the blends can be observed, the viscosity of the blends is more than

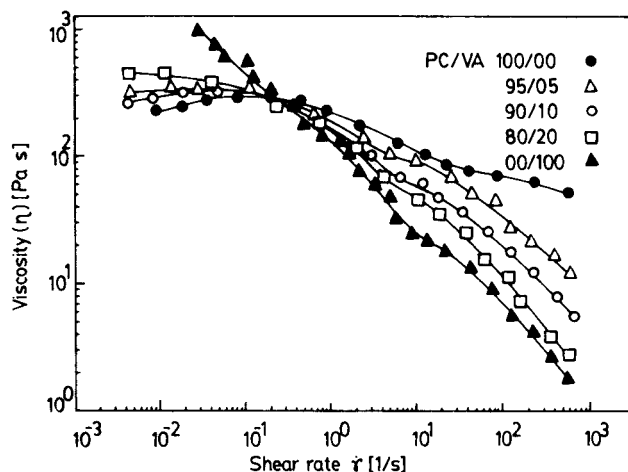


Figure 3 Shear viscosity of the pure components (PC and VA) and their blends (samples injection-molded at 290°C) by parallel-plate rheometry at 290°C.

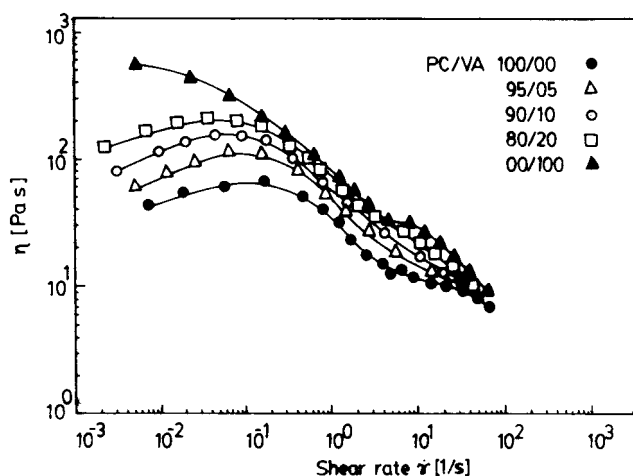


Figure 4 Shear viscosity of the pure components (PC and VA) and their blends (samples injection-molded at 290°C) by parallel-plate rheometry at 300°C.

the viscosity of the pure PC. Also, the viscosity of VA at 300°C is more than the viscosity of pure PC in the entire range of shear rates studied in this work. Thus, at 300°C, the flow curves of the PC matrix and VA do not intersect. However, the viscosities of the blends are again between the viscosities of the neat PC and VA blend components. The analysis of the viscosity behavior of neat PC, VA, and their different blends clearly indicates that the rheological properties of neat PC and VA are favorable for the formation of VA fibrils at 280 and 290°C, as the viscosity ratio of VA to the PC matrix is smaller than unity.

Microstructure development

In this case, to understand the observed rheological behavior of the PC/VA blends, the microstructure development as manifested in the solid state during injection molding was investigated to elucidate the molding temperature, melt rheology, and solid structure relationship. For each PC/VA blend composition, the morphology was studied with respect to the blend processing temperature. However, for the sake of brevity, SEM micrographs of PC/VA blends molded at 290°C, a suitable processing temperature for microfibrillar VA morphology in PC/VA blends, are presented in Figure 7(a–e) (shown later). The microstructure studies were performed on cross-sectional areas of injection-molded bars fractured in liquid nitrogen perpendicularly to the flow direction for both pure PC and PC/VA blends.

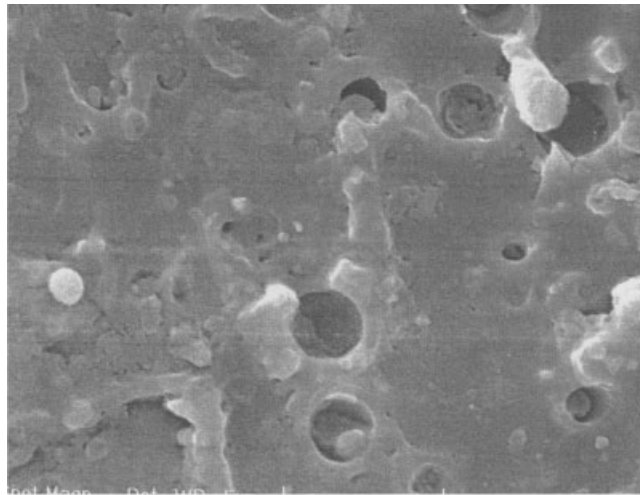
The SEM study of the 95/05 PC/VA blend molded at 280°C revealed that the VA particles were dispersed as small, spherical globules of the order of 0.5–2 μm in the PC matrix. Here the concentration of VA as a dispersed phase was too small to enable coalescence and any possible formation of fibril struc-

tures.^{5,13} Moreover, it was more difficult to deform small droplets than large droplets¹² because of the presence of holes left behind by the VA globules. The 10% VA specimen [Fig. 6(c); shown later] displayed an increased number of nonelongated VA globules. However, the size and nature of the VA domains affected the resultant morphology with increasing VA loading. The 20 wt % VA blend specimen displayed a large number of elongated globules with an enhanced size of 1.0–4.5 μm in the PC matrix along with the formation of a very small amount of a fibrillar structure. Both types of structures are essentially oriented in the injection-molding flow direction.

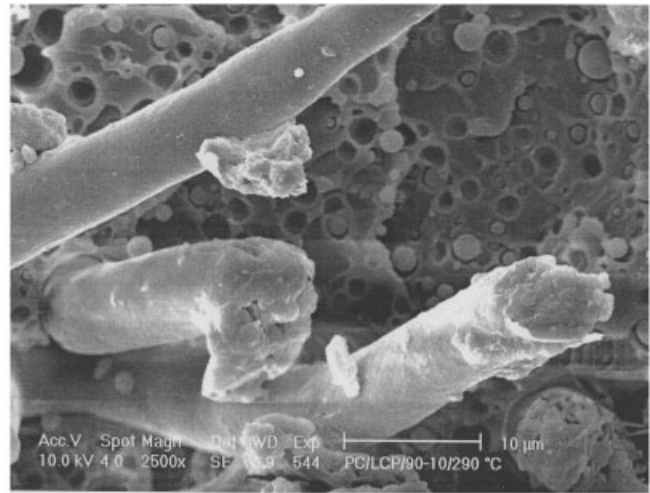
The micrographs shown in Fig. 5 are of fractured standard tensile specimens molded at an injection-molding temperature of 290°C. The morphology observed for the 5 wt % VA blend specimen [Fig. 5(a)] is similar to that observed at 280°C. The 10 wt % VA specimen, however, exhibits the initiation of a skin–core morphology. In this case, the VA particles have an elongated, fibrous appearance in the skin layer [Fig. 5(b)], whereas the core section [Fig. 5(c)] contains mainly spherical VA particles, in addition to a few VA cylinders with nonuniform diameters higher than 3.00–4.00 μm, immersed in a PC matrix. The majority of the spherical particles are nonuniform in their diameter and are at various stages of deformation. The blend morphology with 20% VA can be seen in Figure 5(d,e). The distinct development of a skin–core morphology is now observable. More fibrillation of the VA phase is observed in comparison with a blend with 10 wt % VA. In general, the fibrillation is satisfactory in the skin region and well dispersed [Fig. 5(d)]. The core region, however, indicates the formation of fibrillation of VA along with the well-dispersed spherical globules [Fig. 5(e)]. Such a layered morphology generally develops during injection mold filling, in which the melt at the center of the mold shear-flows with a high velocity and low shear rates and fountain-flows out with high shear rates to the mold wall.⁷ This results in maximum orientation at the mold surface (skin morphology) with a gradual drop in the orientation toward the center (core morphology). In this case, the few VA fibrils seen in the core region could be due to the converging type flow that develops from the tab of a tensile specimen to its narrow neck section.

Once the barrel temperature was raised to 300°C, a marked difference in the morphology was noticed in comparison with the two earlier barrel temperatures. Here, for all the PC/VA blend compositions (5, 10, and 20 wt %), no fibril formation was noticed. The blends exhibited the formation of only spherical droplets of the VA phase, both in the skin region and in the core region.

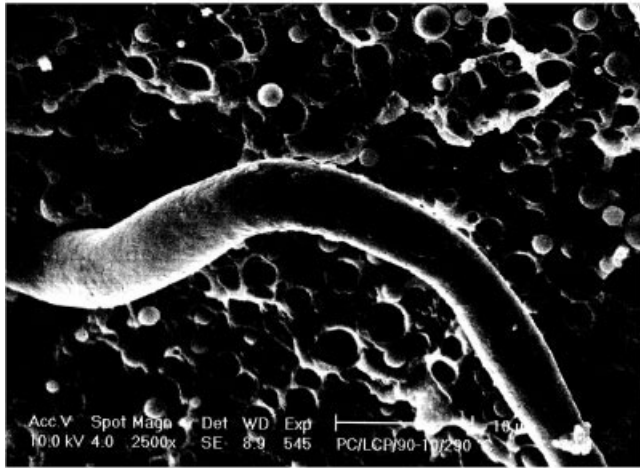
This structural development during injection molding can be related to the rheology–structure relation-



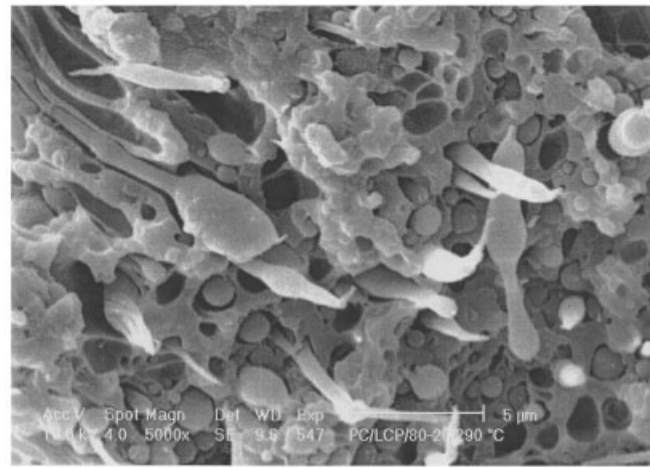
(a)



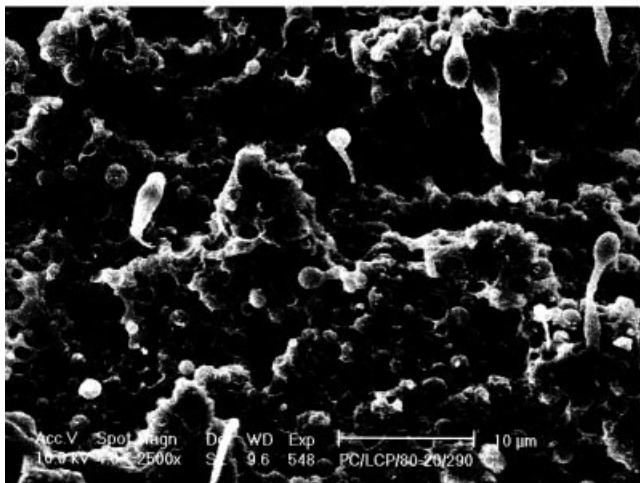
(b)



(c)



(d)



(e)

Figure 5 Morphology of the cryofractured surfaces of the injection-molded PC/VA blends (wt %/wt %) at 290°C: (a) 95/05, (b) 90/10 (skin region), (c) 90/10 (core region), (d) 80/20 (skin region), and (e) 80/20 (core region).

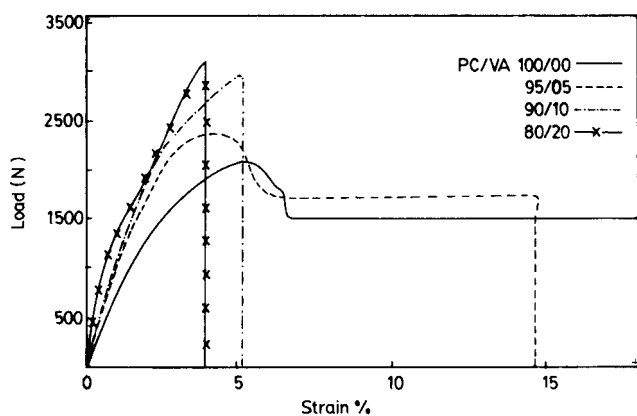


Figure 6 Stress-strain curves of 100/00, 95/05, 90/10, and 80/20 (wt %/wt %) PC/VA blend samples injection-molded at 280°C.

ship. As mentioned previously, LCP fibrillation occurs when the viscosity ratio of the LCP to the polymer matrix is smaller than or closer to unity. It can be observed from Figures 2–4 that the viscosity of the VA phase is less than the viscosity of the matrix PC at higher shear rates. The viscosity of VA at 280°C (Fig. 2) is almost less than the viscosity of PC by an order of magnitude at the shear rate of 100 s^{-1} , whereas at 290°C (Fig. 3), the VA viscosity is less than the PC viscosity by an order of magnitude at the shear rate of 10 s^{-1} . At 290°C, VA is in the nematic phase (crystalline-to-nematic temperature: 282–284°C), but at 280°C, some amount of shear heating is required for it to reach its nematic state. Hence, only a few elongated fibril structures were noticed at 280°C. However, at the molding temperature of 290°C, a good amount of fibrillar structure formation was observed.

At the molding temperature of 300°C, it can be observed from the rheological studies (Fig. 4) that the viscosity of the VA phase is more than the viscosity of the PC phase for all the shear rates studied, and this indicates that the viscosity ratio for VA to PC is

greater than unity. This ultimately prevents the deformation of the VA phase in the blends. Hence, only a spherical droplet morphology has been noticed in the blend specimens molded at 300°C.

In the blends injection-molded at 280, 290, and 300°C, a distinct biphasic nature can be observed, the interphase adhesion being distinctly poor. Many voids can be observed between the VA phase and the PC phase at all compositions and at all molding temperatures, indicating the absence of the VA phase at that position. This resultant morphology clearly indicates immiscibility between the two phases at all compositions studied and at all molding temperatures.

Mechanical properties

Figure 6 shows the stress-strain response of neat PC and PC/VA blend samples molded at 280°C. Neat PC exhibits yield stress and necking followed by homogeneous drawing. Similar behavior can be observed for neat PC samples molded at 290 and 300°C. However, the strain at break decreases with an increasing molding temperature. With the blending of VA with the PC matrix, this necking decreases drastically, even with the addition of only 5 wt % to neat PC. For blends containing 20 wt % VA, the elongation at break decreases to as little as 4%.

The elongations at break of neat PC and PC/VA blend samples obtained at injection-molding temperatures of 280, 290, and 300°C are presented in Table II. With reference to Table II, it can be observed that the elongation at break decreases markedly with increasing VA concentration for the samples molded at 280 (from 22.4% for unblended PC to 3.8% with 20% VA) and 290°C (from 32.4 to 3.0%). However, for the PC specimen molded at 300°C, the elongation at break is lowest (8.2%) and further drops with increasing VA concentration in the blends (3.2% with 20% VA). Therefore, it seems that with an increasing VA con-

TABLE II
Mechanical Properties of Injection-Molded PC and PC/VA Blends at 280, 290, and 300°C as the Processing Temperatures

Mechanical property	Processing temperature (°C)	VA (wt %)			
		0	5	10	20
Elongation at break (%)	280	22.40	11.40	5.10	3.80
	290	32.40	13.70	4.50	3.00
	300	8.20	5.60	4.00	3.40
Tensile modulus (GPa)	280	1.79	2.08	2.20	2.44
	290	1.83	1.90	2.05	2.54
	300	1.75	1.87	1.97	2.31
Tensile strength (MPa)	280	52.50	64.20	68.40	74.80
	290	56.50	61.20	64.00	73.20
	300	55.00	59.80	61.90	68.50
Impact strength (J/m)	280	1055	782	200	91
	290	1091	709	291	73
	300	964	764	164	36

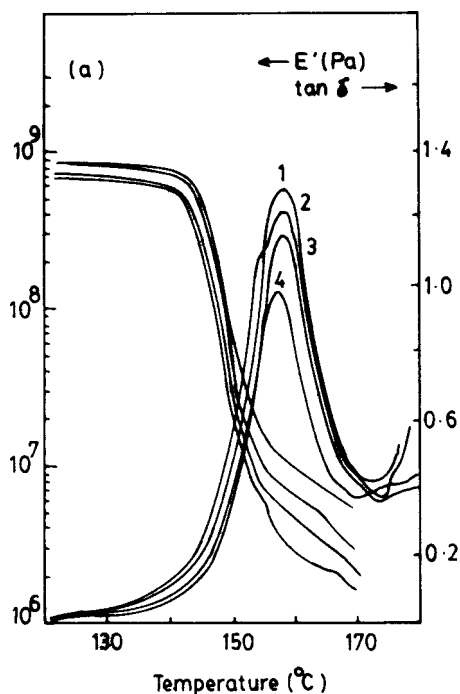


Figure 7 Dynamic mechanical thermal spectra (E' and $\tan \delta$) at a frequency of 1 Hz for injection-molded PC/VA (wt %/wt %) blends at 280°C: (1) 100/00, (2) 95/05, (3) 90/10, and (4) 80/20.

centration and an increasing molding temperature, the blends undergo a ductile transition, being typically brittle, and this results in strain hardening before ductile failure. Also, a more stable neck is formed for the sample molded at 280 and 290°C rather than 300°C, indicating an elongation of the dispersed VA particles. The results are similar to those expected for a short-fiber-reinforced morphology in the tensile direction¹⁹ and in thermoplastic/LCP composites.^{4,34-37}

The variations in the values of the tensile modulus and tensile strength of the PC/VA blends as functions of the sample injection-molding temperature are summarized in Table II. In general, the tensile behavior improves with increasing VA content in comparison with neat PC.

However, the moduli do not follow the rule of mixing because of the different molding-temperature-induced morphologies and, in particular, the poor adhesion between PC and VA in the molded blends.^{3,34-37} The modulus is maximum (2.54 GPa) in the PC/VA blend with 20 wt % VA that was injection-molded at 290°C. This increase in the modulus is almost 1.4-fold (from 1.83 to 2.54 GPa) compared with that of neat PC. This is the material in which maximum fibrillation is observed (Fig. 5). The tensile strength and tensile modulus of the blends injection-molded at 300°C (from 59.60 MPa with 5% VA to 68.50 MPa with 20% VA and from 1.87 GPa with 5% VA to 2.31 GPa with

20% VA, respectively) are less than those of the respective blends at the two other molding temperatures, 280°C (from 64.20 MPa with 5% VA to 74.80 MPa with 20% VA and from 2.08 GPa with 5% at 2.44 GPa with 20% VA, respectively) and 290°C (from 61.20 MPa with 5% VA to 73.20 MPa with 20% VA and from 1.90 GPa with 5% VA to 2.54 GPa with 20% VA, respectively).

As for the notched Izod impact strength, it is well understood that the notched impact strength is associated with the energy dissipation during crack propagation. In this case (Table II), PC/VA blends with increasing VA content show substantial decreases in the impact values (from 1086 J/m for pure PC to 92 J/m for 20% VA samples molded at 290°C). This can be understood by the fact that VA fibers embedded in the PC matrix, as noticed in the morphology studies, have a preferred orientation in the tensile direction as a result of the injection-molding direction. Moreover, the interfacial adhesion is quite poor in these blends. This implies that overall the VA phase tends to reduce the resistance of the matrix polymer, PC, to crack propagation.

Dynamic studies

Figures 7-9 show the variation of $\tan \delta$ with the temperature for the injection-molded PC and its blends with VA samples molded at 280, 290, and 300°C. For a given processing temperature, in the blends, the

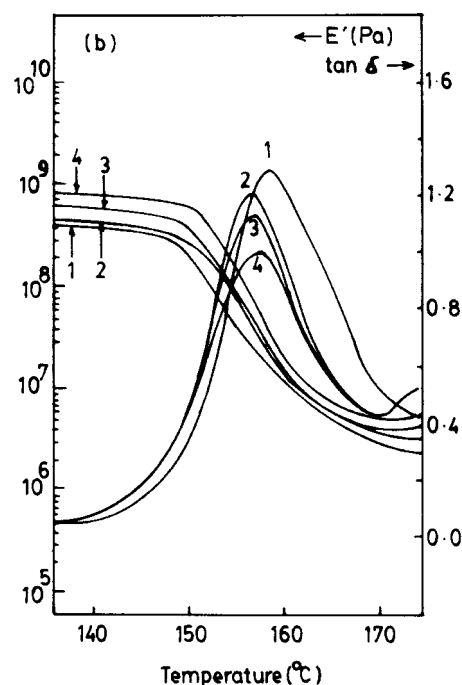


Figure 8 Dynamic mechanical thermal spectra (E' and $\tan \delta$) at a frequency of 1 Hz for injection-molded PC/VA (wt %/wt %) blends at 290°C: (1) 100/00, (2) 95/05, (3) 90/10, and (4) 80/20.

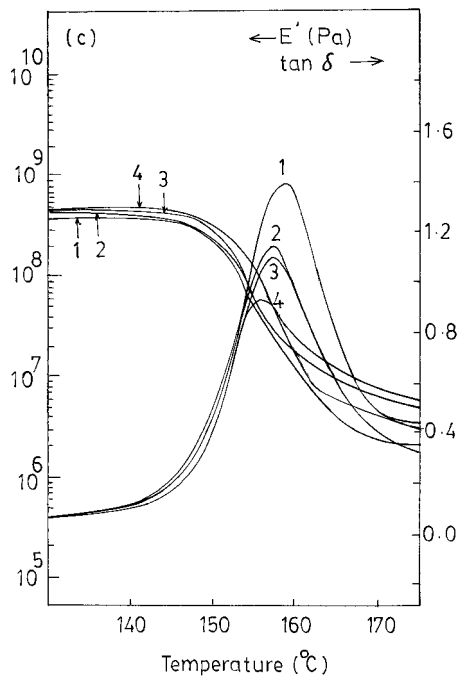


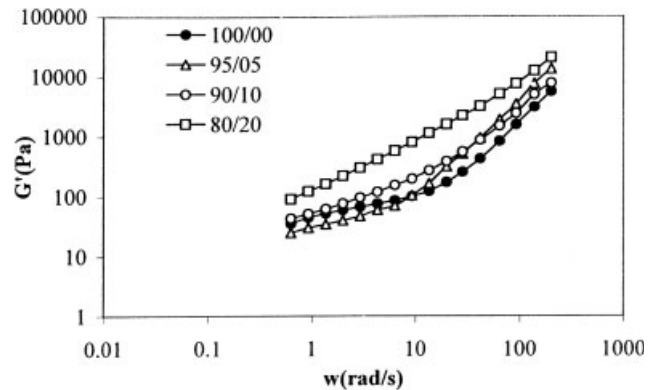
Figure 9 Dynamic mechanical thermal spectra (E' and $\tan \delta$) at a frequency of 1 Hz for injection-molded PC/VA (wt %/wt %) blends at 300°C: (1) 100/00, (2) 95/05, (3) 90/10, and (4) 80/20.

magnitude of $\tan \delta$ and the sharpness decrease with the increase in the VA content. As the loss peaks are indicative of the efficiency of the materials in dissipating mechanical energy, it seems that the PC/VA blends, with decreasing magnitude of the loss peak with increasing VA content, have a lower capacity for dissipating mechanical energy. In this case, this may be attributed to the anisotropic reinforcement of VA. Similarly, with an increasing processing temperature, a blend composition system exhibits lower $\tan \delta$, and this indicates the restricted segmental molecular motions at the interface. Also, at a high concentration, strong agglomeration of VA particles is expected to occur that cannot be easily broken by applied forces. As a result, PC/VA composites exhibit in general enhanced modulus in comparison with pure PC. In such cases, the low particle–particle friction results in a lowering of the $\tan \delta$ peak magnitude. In other words, now the moments of the PC chain segments are hindered because of the larger VA domains. This results in an increase in the stiffness of both the PC and VA phases in the composites.

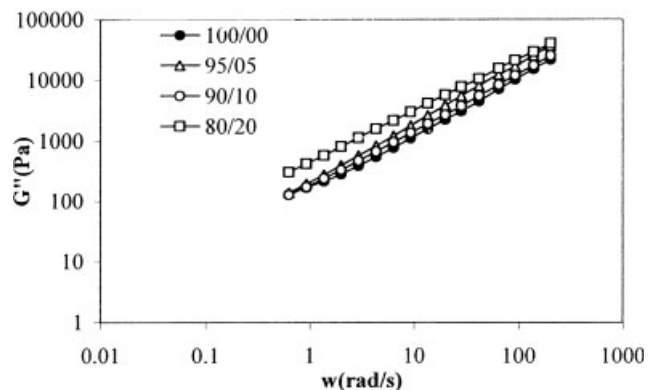
Figures 7–9 also show the variation of the dynamic tensile storage modulus (E') for the pure PC and its blends with VA. The pure PC exhibits a decrease in the value of E' at the glass-transition temperature region corresponding to the temperature range of 145–150°C. Blends containing higher VA concentrations show a comparatively less steep fall in the modulus value in this region. Similarly, a shift in the pla-

teau to higher modulus magnitudes can be observed in the blends, indicating the gradual formation of the VA domain morphology in the PC matrix. Although the addition of VA to PC increases the modulus with the processing temperature increasing from 280 to 290°C, comparatively it decreases for the blend processed at 300°C. This is a result of the processing-temperature-induced microfibril morphology that develops at 280 and 290°C. The reinforcement effect, however, is pronounced in the composites, as shown by the enhanced modulus (Figs. 7 and 8), with the increasing VA concentration.

The viscoelastic properties of the molten polymer/LCP composites and then their ability to subsequently freeze the resultant morphology are pertinent to processing. In the context of the mechanical properties, the melt elasticity, a widely used parameter in polymer processing, is related to changes in the magnitudes of the viscoelastic functions, mainly the shear storage modulus (G') and shear loss modulus (G'').³⁸ Additionally, these dynamic responses are related to molecular relaxation processes of the composite materials, which are again influenced by the morphology



(a)



(b)

Figure 10 Dynamic viscoelastic properties of PC/VA blends injection-molded at 280°C by parallel-plate rheometry at 280°C: (a) G' and (b) G'' .

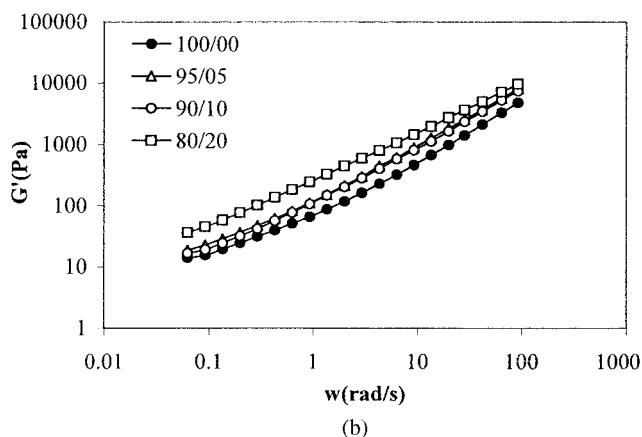
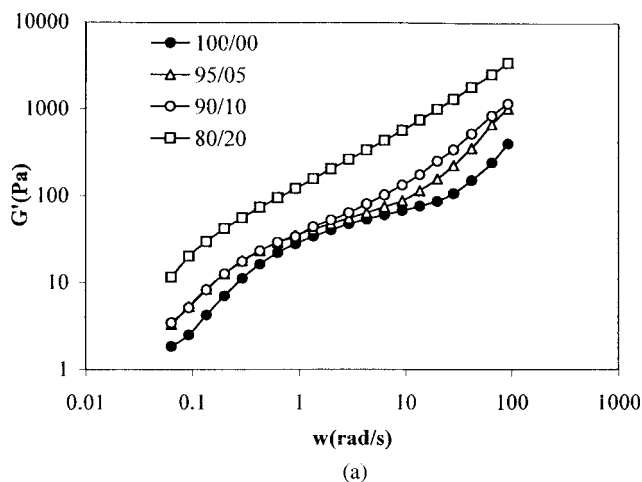


Figure 11 Dynamic viscoelastic properties of PC/VA blends injection-molded at 290°C by parallel-plate rheometry at 290°C: (a) G' and (b) G'' .

and composition of the composites and interfacial adhesion.

Figures 10–12 show the frequency dependence of G' and G'' of pure PC and its composites with VA and cover the terminal and plateau regions of relaxation behavior. In the middle-order frequency region, pure PC displays a G' rubbery plateau for all three samples processed at 280, 290, and 300°C. This behavior is similar to that observed for a flexible, entangled polymer melt and manifests the presence of a strong elastic network. In the pure PC, it seems that this entanglement density decreases little with an increasing processing temperature. However, the disappearance of this plateau in a high shear frequency region indicates a homogeneous PC melt. In the case of the PC/VA systems, the melt behavior is a dominating function of the VA loading rather than the processing temperature. It appears that the network structures observed in the pure PC collapse with increasing VA content in the PC/VA composites at all three processing temperatures. Consequently, now the melt state in the composites becomes isotropic and homogene-

ous. Finally, the system reaches a terminal relaxation zone at low shear frequencies. This observed decrease in the G' plateau with increasing VA content in the PC/VA composites ultimately facilitates the orientation of VA fibrils.

Except for the composites processed at 280°C with 5 wt % VA in the low-frequency region, all the composite samples processed at 280, 290, and 300°C, exhibited values of G' higher than those of the pure PC. The overall reinforcing effect of VA led to these enhanced moduli. The relative magnitude of G' not only is a function of the processing temperature but also depends on the weight percentage of VA in the composites, and this makes the shearing force situation more complex. The G' magnitude for the samples increases, moving from 300 to 290°C and then to 280°C as the composite processing temperatures. Similarly, the increasing reinforcing effect of the VA component on the PC matrix is pronounced in a low-frequency region for 280°C processed samples, whereas, it is in a high-frequency region for 290°C samples, particularly with 20 wt % VA in the composites. Otherwise, increasing the VA content in the composites

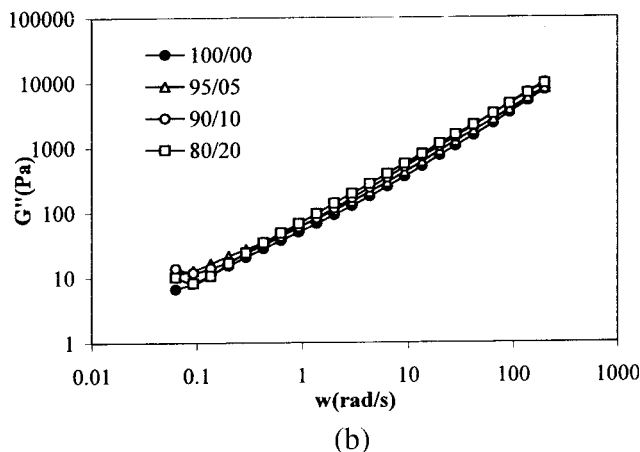
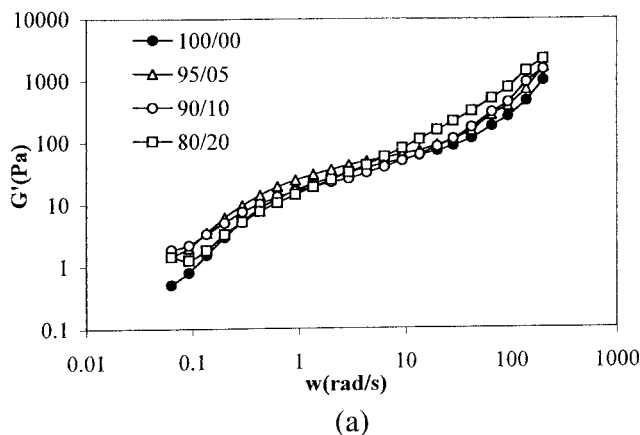


Figure 12 Dynamic viscoelastic properties of PC/VA blends injection-molded at 290°C by parallel-plate rheometry at 300°C: (a) G' and (b) G'' .

increases the magnitude of G' as one in general expects for a linear composition reinforcement correlation. It is generally recognized that in a low-temperature melt there are more entanglements at low shear rates, so now chain interactions play a dominant role, resulting in higher G' values. However, as the shear rates and the temperature of the melt increase, these entanglements decrease, and this lowers the modulus.

The G'' values also show a monotonic increase at all frequencies with increasing VA content and are higher than the G' values over the entire frequency range. These high G'' values for the composites reflect the longer relaxation times. The rigid-rod-like VA structure and extent of entanglement contribute to this response. For the composites, however, the G'' values begin to fall with increasing composite processing temperatures from 280 to 290 and then to 300°C, resulting in shorter relaxation times. This may be attributed to relaxed long-range movements of the PC molecules in the composites.

CONCLUSIONS

We have demonstrated that during melt blending in an injection-molding process, the morphology of amorphous/crystalline immiscible polymer blends depends on the injection-molding temperature (barrel temperature) in comparison with the melting temperature of the crystalline polymer component, the molding-temperature-dependent viscosity ratio of the blend, and the blend composition. The addition of an immiscible VA phase improves the melt processing of PC. The experimental results show that as the viscosity of PC/VA blends varies with the shear rate and the injection-molding temperature, the developing morphology can change accordingly in the molding process. By the use of a suitable processing temperature (280 and 290°C) in the molding process, the VA phase favorably elongates to develop a microfibrillar morphology in PC/VA blends. This structure development can be attributed to the rheological behavior: at 280 and 290°C, the viscosity of the VA phase is lower than the viscosity of the matrix PC at high shear rates. At a higher processing temperature (300°C), the PC viscosity is lower in most of the shear rate range compared with that of the VA component, and this results in unfavorable conditions for fiber formation.

The shear viscosity and dynamic viscoelastic properties, G' and G'' , of the VA-filled PC melts were studied. As uniformly dispersed composite systems, the PC composites with 20 wt % VA and a 290°C injection-molding processing temperature exhibited higher dynamic moduli. The fibrillar structure development was manifested in the enhanced mechanical properties. The barrel temperature of 290°C in the

injection-molding process had the most significant effect on the amount and orientation of the VA fibrillar domains, which ultimately affected the mechanical property enhancement in the PC/VA self-reinforcing composites. The viscoelastic melt behavior analysis suggests that the addition of VA increases the relaxation time of PC in composites.

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