

**Full Paper:** The tetrafunctional epoxy resin, tetraglycidyl-4',4'-diaminodiphenyl methane (TGDDM), has been investigated as an efficient reactive compatibilizer for the blends of polyarylate (PAr) with a liquid crystalline polymer (LCP). TGDDM can react with PAr and LCP at the interface simultaneously to produce the PAr-co-TGDDM-co-LCP mixed copolymers during melt blending. These copolymers tend to anchor along the interface as the result of the interfacial reaction and thus serve as effective compatibilizers to reduce the interfacial tension and to enhance the interfacial adhesion in the solid state. The morphologies of the PAr/LCP blends were inspected by means of scanning electron microscopy (SEM). It is observed that the dispersed LCP phase domains reduce obviously after compatibilization. Furthermore, it is also found that the reduced interfacial tension caused by the addition of TGDDM plays a vital role in affecting the deformation of the LCP phase domains in the compatibilized PAr/LCP blends. The LCP phase tends to deform into greater numbers and finer fibrils with high aspect ratio after the addition of TGDDM in those blends containing adequate LCP content (>10%). In the blend containing low amount of LCP (Par / LCP = 95/5) with high TGDDM content (0.3 phr or higher), however, the LCP phase can only exist as fine but short fibrils or even ellipsoids. The overall mechanical properties of the PAr/LCP blends are substantially improved after compatibilization by this coupling-type reactive compatibilizer. The generation of LCP fibrils with high aspect ratio and improved interfacial adhesion are the two hinges to enhance the performance of the compatibilized PAr/LCP blends.



(D) PAr/LCP/TGDDM=80/20/0.5

SEM micrograph of the cryogenically fractured surface of the PAr/LCP = 80/20 blend containing the indicated amount of TGDDM, parallel to the flow direction of the injection-molded specimen and the skin region.

## Morphologies and mechanical properties of polyarylate/liquid crystalline polymer blends compatibilized by a multifunctional epoxy resin

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### Introduction

Thermotropic liquid crystalline polymers (LCPs) possess special rheology properties, so polymer blends of thermoplastics (TPs) with a minor LCP content have attracted considerable attentions since the early 1980s. The LCP can function as a processing aid by reducing the viscosity of the matrix material. In addition, the LCP phase domains in a TP/LCP blend can be deformed into elongated fibrils under shear flow to act as *in situ* composites to reinforce the TP matrix.<sup>[1–3]</sup> However, it has been found that the

deformation of the dispersed LCP phase into elongated fibrils in melt process is very complicated. The mechanical properties of the eventually produced TP/LCP blends are highly dependent on the morphology of the LCP phase, which is controlled by several factors such as the rheological and interfacial properties of the blend components, processing methods and conditions, and the blend composition. In some cases, the LCP domains cannot be deformed into fibrils under shear and appear in spherical droplets or ellipsoids instead,<sup>[4,5]</sup> and the reinforcing effect

on enhancing the mechanical properties of these blends is limited. Based on these understandings, it is evident that the generation of the *in situ* LCP fibrils by using appropriate processing conditions is the key to achieve the desirable reinforcement for TP/LCP blends.

Except for a few pairs, most TP/LCP blends are immiscible and incompatible due to the conspicuous difference in chemical structures. Therefore, the adhesion between the phases of two constituents is poor and the mechanical properties are often lower than those predicted by the rule of mixture. In order to improve the interfacial adhesion of a TP/LCP blend, the solution seems to be obviously simple by employing an appropriate compatibilizer during the melt blending, a common approach for the compatibilization of TP/TP blends. The techniques of compatibilizing TP/TP blends, by either reactive or non-reactive compatibilizers, are well developed today and have been published in several reviews.<sup>[6–10]</sup> A well-compatibilized TP/TP blend can be characterized by a better processability, finer and stable morphology, increased interfacial adhesion in the solid state, and improved mechanical properties. For compatibilized TP/LCP blends, however, most of them result in lower quantities of the *in situ*-formed LCP fibrils with a lower aspect ratio as compared to the corresponding uncompatibilized counterparts, or even convert the LCP fibrils into droplet domains.<sup>[11,12]</sup> The overall mechanical properties, in general, are improved after compatibilization; however, the extent of improvement is not very substantial.

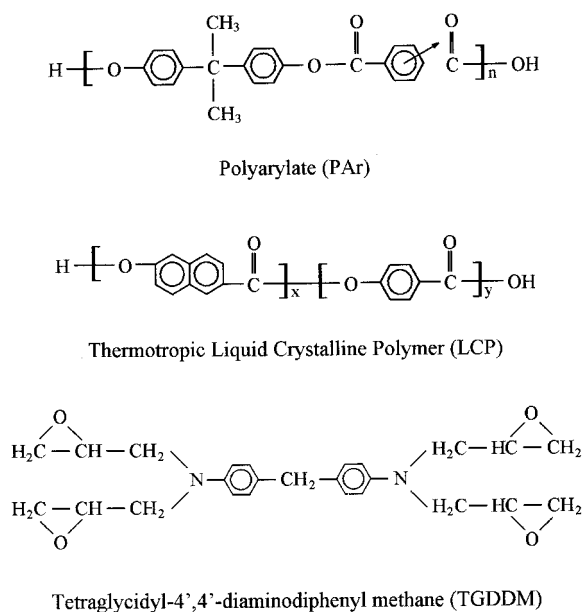
In our previous investigations, it was found that using a low-molecular-weight multifunctional coupling agent can be a better approach than a conventionally reactive compatibilizer to compatibilize a TP/LCP blend.<sup>[13,14]</sup> This multifunctional coupling agent has the opportunity to react with both base polymers simultaneously to give *in situ*-formed copolymers. These interfacially formed copolymers tend to reside at the interface preferentially and function as effective compatibilizers because they possess segments with identical structures respective to the two blend constituents. In addition, these compatibilized TP/LCP blends have greater numbers of the *in situ*-formed LCP fibrils with high aspect ratios relative to the uncompatibilized ones.<sup>[13,14]</sup> Subsequently, these compatibilized TP/LCP blends exhibit drastic improvements on mechanical properties, both the stiffness and toughness. Although it looks very promising to combine the two blend components through a suitable coupling agent, several criteria have to be satisfied when using a coupling agent as a reactive compatibilizer. Firstly, both base polymers must possess the necessary functional groups that are capable of chemical reactions with the coupling agent. Furthermore, the relative reactivity of the coupling agent toward blend constituents must be comparable. Secondly, the relative miscibility between the coupling agent and the base polymers has to be considered. The most desirable coupling agent is actu-

ally the one that is incompatible with both blend components. The incompatibility causes the coupling agent to be forced to reside at the interface, and consequentially this coupling agent has the best opportunity to react with both constituents simultaneously to produce the desirable copolymers. Thirdly, the melting sequence of the blend components is also an important factor affecting the resultant chemical reaction during the process of melt blending. A coupling agent usually possesses a lower melting temperature relative to the blend components and therefore tends to mix with the first melted component regardless of the relative compatibility. The detailed compatibilization mechanism by a coupling agent has been discussed in our previous reports.<sup>[13,15]</sup>

Polyarylate (PAr), made from bisphenol-A and isophthalic/terephthalic acids, is an amorphous aromatic polyester with high heat distortion temperature (HDT), excellent electric and mechanical properties, flame resistance, and ultraviolet resistance.<sup>[16]</sup> However, PAr also possesses some shortcomings during the melting process, such as high melt viscosity, high processing temperature, and narrow temperature range for processing. Therefore, the addition of small amounts of LCP should be able to reduce the melt viscosity of the PAr matrix and results in the improvement of processability. Similar to any polyester pairs, an ester interchange reaction is expected to occur between PAr and the copolyester LCP. Nevertheless, it was proved that the ester interchange reaction between PAr and LCP is insignificant and can be neglected during melt blending.<sup>[17]</sup> Kiss<sup>[18]</sup> has studied the mechanical properties of PAr/LCP blends and found that the greatest improvement is achieved when the LCP content is 30%. Kim et al.<sup>[19]</sup> employed a commercially available block copolyesterether Hytrell 7246, a product of Du Pont, as a non-reactive compatibilizer for the PAr/LCP blends and resulted in decreased dynamic viscosity, better interfacial adhesion, and improved mechanical properties. A tetrafunctional epoxy resin, tetraglycidyl-4',4'-diaminodiphenyl methane (TGDDM), has been demonstrated as an efficient coupling agent in compatibilizing the blends of poly(ethylene terephthalate) (PET) and LCP,<sup>[14]</sup> resulting in generating greater numbers of LCP fibrils with a higher aspect ratio, stable morphology, and substantial improvements on mechanical properties. Consequently, the aim of this study is to improve the compatibility and mechanical properties of the PAr/LCP blends by using TGDDM as a reactive compatibilizer.

## Experimental part

PAr, Ardel D-100, was purchased from Union Carbide Corp. of USA. It is a copolyester of bisphenol-A with a mixture of isophthalic/terephthalic acids (50/50). The LCP is an aromatic random copolyester consisting of 73% 4-hydroxybenzoic acid and 27% 2-hydroxy-6-naphthoic acid supplied by Hoechst Celanese as Vectra A900. The tetrafunctional epoxy resin, tet-



Scheme 1. The chemical structures of materials.

raglycidyl-4',4'-diaminodiphenyl methane (TGDDM), was obtained from Ciba-Geigy of Switzerland. The chemical structures of materials are presented in Scheme 1.

In order to prevent the polyesters from hydrolysis during the process of melt blending, both PAR and LCP were dried at 120 °C for over 24 h while the TGDDM was dried at 60 °C for over 8 h in separate ovens prior to extruder compounding. All blends were prepared in a 30 mm co-rotating twin-screw extruder by maintaining the barrel temperature in the range of 320–340 °C and the screw speed at 260 rpm. The extruded pellets were dried at 120 °C for over 10 h and then molded into standard ASTM specimens by an Arburg 3 oz injection-molding machine.

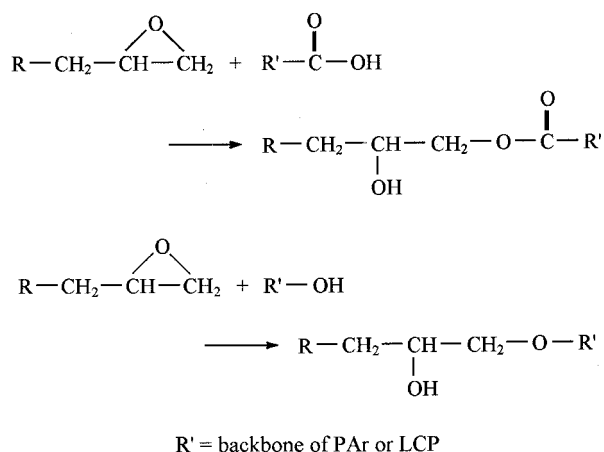
Torque versus time behavior was obtained by a Brabender Plasti-Corder at 300 °C and 30 rpm without nitrogen purge. Melt flow rates (MFRs) of base polymers and blends were measured at 340 °C with a 2.16 kg loading by an automatic flow rate timer from Ray-Ran Co. of Britain. The capillary rheological measurements were carried out at 300 °C using a capillary rheometer (L/D = 40, orifice radius = 0.02 inch) from Kayeness Co. of USA.

Morphologies of the cryogenically fractured surfaces of the injection-molded specimens were examined from the core to skin regions, perpendicular and parallel to the flow direction, by scanning electron microscopy (SEM). Standard tensile tests were conducted by following the ASTM-D638 method at ambient conditions with crosshead speed of 5 mm/min. Unnotched Izod impact strengths were measured at ambient conditions according to the ASTM-D256 method.

## Results and discussion

### Chemistry

The reactive compatibilization has been regarded as a better approach than the non-reactive system to improve



Scheme 2. Summarized reaction mechanisms of the epoxy group with carboxyl and hydroxyl groups.

the compatibility of polymer blends. A reactively *in situ*-formed compatibilizer can be considered as a nonspecific type compatibilizer because the structure and quantity of the eventually formed copolymers are nonspecific and dependent on many factors such as the concentration of the reactive group, the temperature, the mixing time, the reactivity, the catalyst, and the melting sequence. Several multifunctional coupling agents possessing relatively low molecular weight have been employed successfully as reactive compatibilizers for many blending systems.<sup>[13–15, 20–24]</sup> The low-molecular-weight TGDDM is able to migrate rapidly between phases in the PAR/LCP blend during melt blending and has therefore the opportunity to react with PAR and LCP simultaneously at the interface to form the PAR-*co*-TGDDM-*co*-LCP mixed copolymers. The reaction mechanisms of the epoxy group of TGDDM with the carboxyl and hydroxyl groups of polyesters are well established<sup>[25]</sup> and summarized in Scheme 2. Indeed, not all the added TGDDM is able to react with PAR and LCP simultaneously. A portion of the added TGDDM may act as chain extender to react with only one constituent, producing highly branched copolymers or even a crosslinked network. Evidently, such products cannot serve as compatibilizers in the PAR/LCP blends. Certain fraction of the added TGDDM can react with PAR and LCP simultaneously at the interface to produce the PAR-*co*-TGDDM-*co*-LCP mixed copolymers during melt blending. These interfacially formed copolymers, which are the most desired in this PAR/LCP blending system, tend to anchor along the interface to serve as effective compatibilizers.

### Torque versus time

Fig. 1 presents the torque curves as a function of mixing time at 300 °C for the pure PAR, LCP, and the PAR/LCP = 90/10 mixtures containing various amounts of

TGDDM. Pure PAr exhibits high torque values (Fig. 1 b), about five times higher than the pure LCP (Fig. 1 a) under the same test conditions. The torque values of both PAr and LCP decline gradually with mixing time, probably due to the slight hydrolytic degradation caused by the contact with air moisture during testing. Torque values of the PAr/LCP = 90/10 mixture (Fig. 1 c) lie between those of PAr and LCP as would be expected. When 0.1 phr TGDDM is added in the PAr/LCP = 90/10 mixture, the torque value exhibits a noticeable increase relative to that of the uncompatibilized one (Fig. 1 d versus 1 c). As mentioned previously, the TGDDM molecule can act as a chain extender or a coupling agent in PAr/LCP blends to produce various copolymers with high molecular weight, and these copolymers enable to contribute to the observed viscosity increase in the compatibilized blends. Both, the increased molecular weight and interfacial friction, are responsible for the viscosity increase in the compatibilized blends, but the individual contributions are not easily distinguishable. For the uncompatibilized blends under shear stress, a “slide” between phases of two incompatible polymers takes place easier because of a higher interfacial tension and a lower interfacial friction and results in the lower viscosity. Since the *in situ*-formed PAr-co-TGDDM-co-LCP copolymers, which are produced by the coupling reaction of TGDDM at the interface, tend to anchor along the interface due to the possession of identical structures to the blend constituents, they can function as interfacial adhesion promoters and raise the interfacial friction under shear. Hence, the compatibilized PAr/LCP = 90/10 mixture exhibits a higher viscosity relative to the uncompatibilized one. Furthermore, the torque value of the compatibilized PAr/LCP = 90/10 mixtures increases with the increase of the TGDDM content

as presented in Fig. 1 d and 1 e. The higher viscosity of the better-compatibilized blend illustrates that both molecular weight and interfacial friction increase progressively as the quantity of TGDDM is increased.

*Processability and capillary rheometry*

Adding a LCP into a TP matrix can reduce the melt viscosity that has been well recognized, and thus the TP/LCP blends can be processed with lower energy expenditure. Nevertheless, problems usually accompany the process of melt blending such as the incompatibility induced die swelling and the melt fracture. These processing problems become more apparent, especially when the blend contains a high LCP content. In general, the extruder blending of PAr/LCP blends in this study has been processed fairly smooth and easy even without the addition of TGDDM. Only the uncompatibilized blend containing higher LCP content (20%) did experience minor processing problems, but these problems essentially disappeared after the compatibilization. The extruder power outputs required for the entire blend compositions are listed in Tab. 1. The extruder current of the uncompatibilized PAr/LCP blend decreases with the increase of the LCP content as would be expected. On the other hand, the addition of TGDDM in the PAr/LCP blends results in a slight increase in the extruder current, indicating the viscosity increase of the compatibilized blends. This viscosity increment can be attributed to the occurrence of chemical reactions between TGDDM and the two base polymers during melt blending. The effect of TGDDM content on the reduction of die swelling ratio of the PAr/LCP blends is shown in Fig. 2. It is clear that the die swelling ratio has been reduced substantially with the increase of the

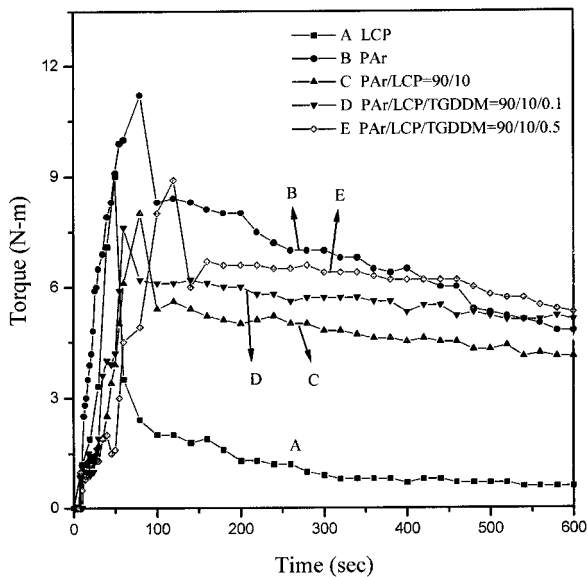


Fig. 1. Plots of torque versus time for base polymers and mixtures of selected compositions at 300 °C and 30 rpm.

Tab. 1. Extruder currents and melt flow rates of PAr/LCP/TGDDM blends.

| Composition               | Extruder current | MFR <sup>a)</sup> |
|---------------------------|------------------|-------------------|
|                           | Amp              | g/10 min          |
| PAr                       | –                | 2.2               |
| LCP                       | –                | 67.2              |
| PAr/LCP = 95/5            | 27               | 4.2               |
| PAr/LCP/TGDDM = 95/5/0.1  | 29               | 2.8               |
| PAr/LCP/TGDDM = 95/5/0.3  | 29               | 2.5               |
| PAr/LCP/TGDDM = 95/5/0.5  | 30               | 2.3               |
| PAr/LCP = 90/10           | 25               | 6.9               |
| PAr/LCP/TGDDM = 90/10/0.1 | 27               | 4.2               |
| PAr/LCP/TGDDM = 90/10/0.3 | 27               | 3.1               |
| PAr/LCP/TGDDM = 90/10/0.5 | 29               | 2.8               |
| PAr/LCP = 80/20           | 20               | 8.4               |
| PAr/LCP/TGDDM = 80/20/0.1 | 22               | 6.0               |
| PAr/LCP/TGDDM = 80/20/0.3 | 23               | 4.7               |
| PAr/LCP/TGDDM = 80/20/0.5 | 24               | 3.3               |

<sup>a)</sup> Tested at 340 °C with a 2.16 Kg loading.

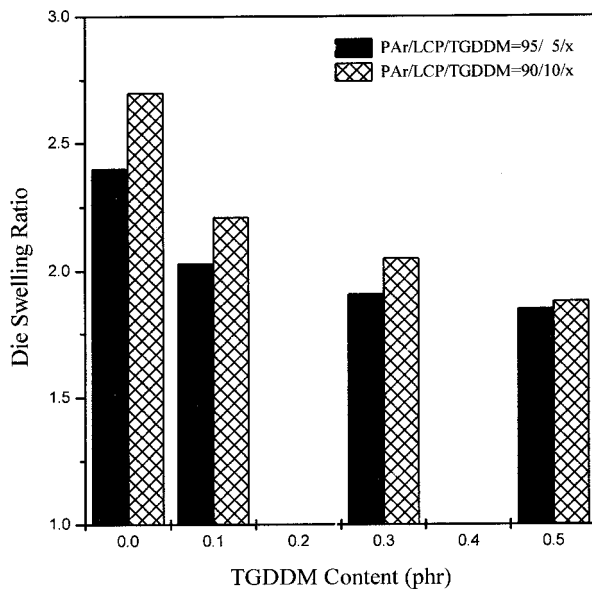


Fig. 2. Die swelling ratio of the PAr/LCP/TGDDM blends as function of TGDDM content.

TGDDM content. The extrudate swelling is resulted from the shape recovery of the dispersed phase. Thus, the blend with a higher elasticity corresponds to the higher extrudate swelling.<sup>[26]</sup>

Tab. 1 also lists the resultant MFRs of the PAr/LCP/TGDDM blends with all the compositions studied. The pure PAr exhibits a MFR of 2.2 at 340°C that is significantly lower than that of the pure LCP (67.2), illustrating the large viscosity difference between these two polymers. Adding TGDDM into the PAr/LCP blends leads to the MFR reduction as compared with the uncompatibilized ones, and the MFR of the compatibilized blend decreases

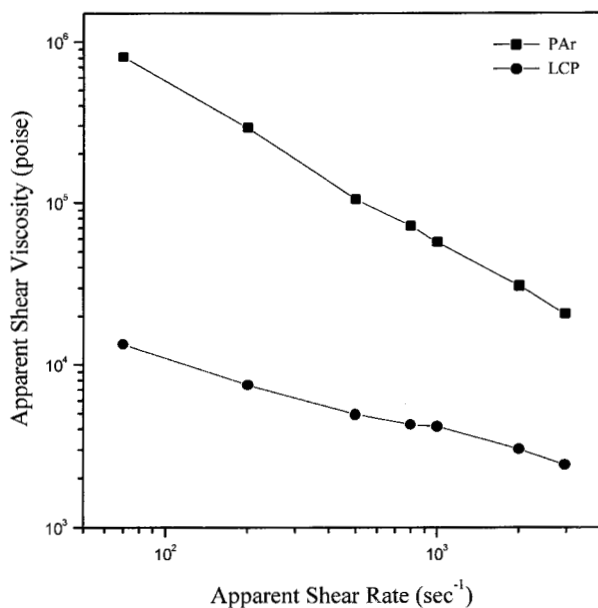


Fig. 3. Variations of shear viscosity with shear rates for pure PAr and LCP at 300°C.

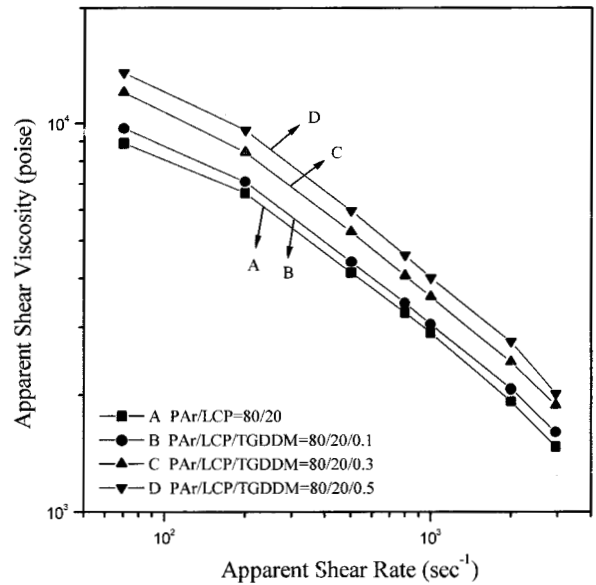


Fig. 4. Plots of shear viscosity versus shear rate for PAr/LCP = 80/20 blends containing various amounts of TGDDM at 300°C.

gradually with increasing the TGDDM content as expected.

Fig. 3 shows the variations of shear viscosity with shear rates for pure PAr and LCP at 300°C. It is clear that the PAr possesses a significantly higher viscosity than that of the LCP under the same test conditions. For facilitating the formation of LCP fibrils in blends, it is generally considered that the component LCP should have a lower viscosity relative to the host matrix. The shear viscosity versus the shear rate behavior for the PAr/LCP = 80/20 blends, uncompatibilized and compatibilized, are given in Fig. 4. For the compatibilized PAr/LCP = 80/20 blends, the presence of 0.1 phr TGDDM results in a substantial viscosity increase as shown in Fig. 4b, and the viscosity increases progressively with increasing the amount of TGDDM (Fig. 4c and 4d). The increase of viscosity can be attributed to the molecular weight increase and the enhancement of interfacial friction as discussed previously.

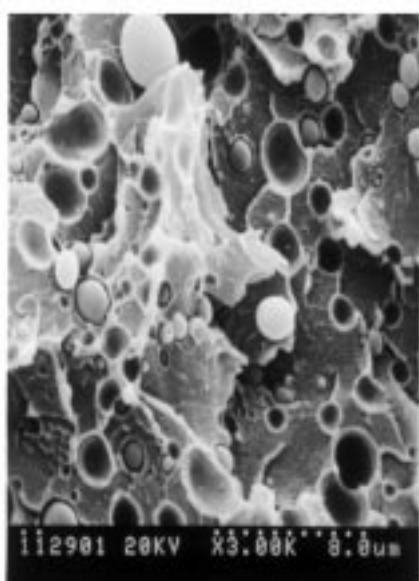
### SEM morphologies

The interfacial properties of blends play an important role in determining the degree of dispersion of the minor phase and the resultant mechanical performance.<sup>[22, 27–33]</sup> For blends containing LCP, interfacial properties also affect the deformation of *in situ*-formed fibrils.<sup>[27, 30]</sup> Therefore, observing the morphology evolution, which is greatly affected by interfacial properties, is important to understand the mechanical properties of blends. A blend composed of two immiscible polymers can usually be characterized by the large dispersed phase domains and coarse morphology due to high interfacial tension. In gen-

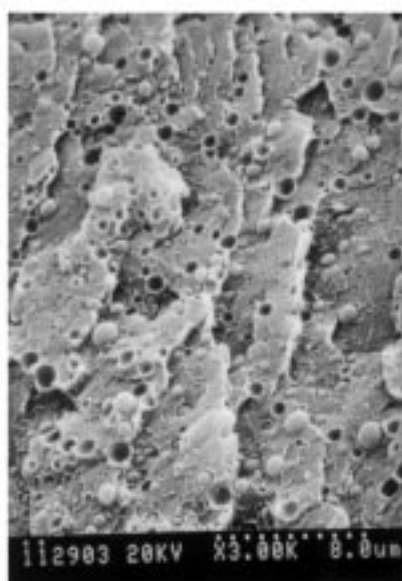
eral, the coarse morphology can be improved by the addition of a suitable compatibilizer. The employed compatibilizer, reactive or non-reactive, tends to concentrate at the interface and functions as an interfacial emulsifier to lower the interfacial tension and leads to smaller dispersed phase domains. In addition, the presence of a compatibilizer also stabilizes the fine phase domains against coalescence.<sup>[29]</sup> The effect of compatibilization on the morphology of the PAr/LCP blends is shown in Fig. 5. The uncompatibilized PAr/LCP blends, as presented in Fig. 5a and 5c, exhibit relatively larger dispersed and spherical LCP phase domains at the core region, a typical morphology of blends comprising two incompatible polymers. With the presence of TGDDM, the domain size of

the dispersed LCP phase reduces substantially and evenly as presented in Fig. 5b and 5d, illustrating the improvement of the compatibility of the PAr/LCP blends. The formation of the *in situ* compatibilizers at the interface during melt blending leads to the reduction in the interfacial tension and stabilization against droplets coalescence. In addition, these copolymers are responsible also for the enhancement of interfacial friction in the melt and interfacial adhesion in the solid state.

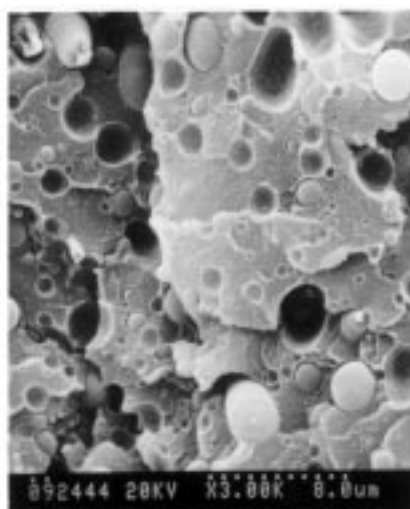
Taylor<sup>[34]</sup> studied the deformation of a single Newtonian droplet suspended in a Newtonian matrix, and nowadays his theory has been used extensively to describe the deformation of a LCP phase in TP/LCP blends.<sup>[30,35]</sup> According to Taylor, the deformation of a spherical dro-



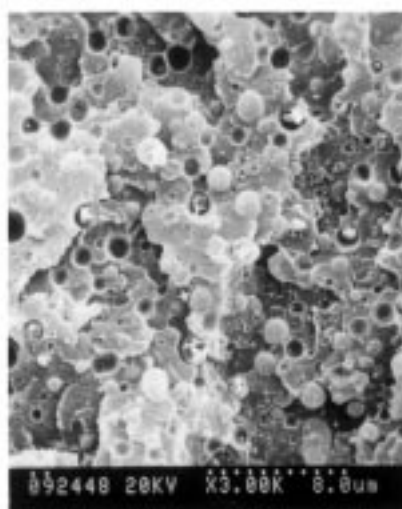
(A) PAr/LCP=90/10



(B) PAr/LCP/TGDDM=90/10/0.3



(C) PAr/LCP=80/20



(D) PAr/LCP/TGDDM=80/20/0.3

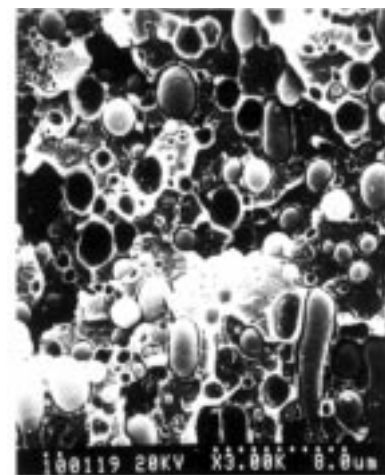
Fig. 5. SEM micrographs of the cryogenically fractured surfaces of the uncompatibilized and compatibilized PAr/LCP blends, perpendicular to the flow direction of the injection-molded specimen and at the core region.

plet with an initial radius  $D$  in simple shear or elongational flow depends on the viscosity ratio of the droplet phase ( $\eta_d$ ) to the matrix ( $\eta_m$ ),  $\eta_r = \eta_d/\eta_m$ , shear rate ( $\dot{\gamma}$ ), and interfacial tension ( $\sigma$ ). Hence, the deformation can be expressed as the following equation:

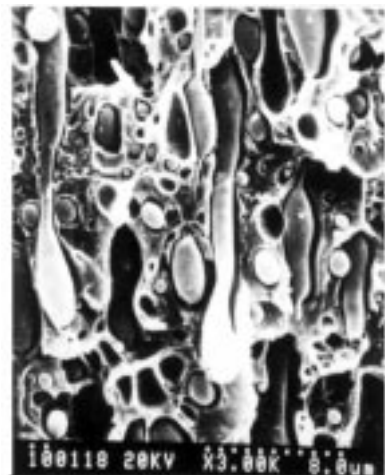
$$\frac{L-B}{L+B} = \frac{\dot{\gamma}\eta_m D}{\sigma} \left( \frac{19\eta_r + 16}{16\eta_r + 16} \right) \quad (1)$$

where  $L$  and  $B$  are the length and breadth of the deformed droplet, respectively. Eq. (1) indicates that the viscosity ratio and the supplied shear rate are the two factors affecting the droplet deformation in a blend. A fibrillar morphology is favored in a TP/LCP blend when  $\eta_r$  is smaller or close to unity,<sup>[36]</sup> and a moderately high shear rate is able to facilitate the generation of a filament structure.<sup>[37]</sup> Consequentially, the LCP phase in a TP/LCP blend usually exhibits an unique “skin-core” morphology perpendicular to the flow direction of the injection-molded specimen, i.e. the through-thickness direction, due to the flow kinematics. Highly oriented LCP fibrils are formed close to the skin region resulting from the elongational flow at the advancing flow front, whereas at the core region, a less oriented LCP phase is usually observed arising from the relatively lower shear flow in the center of the mold.<sup>[38]</sup> The variations of the deformation of the LCP phase with locations of the through-thickness direction of the injection-molded specimen for the PAr/LCP = 80/20 blend were examined by SEM and are displayed in Fig. 6. The samples were cryogenically fractured along the principle direction of flow. At the core region, as presented in Fig. 6a, the LCP phase domains are mainly in spherical and a few ellipsoidal droplets because the shear stresses are not strong enough to overcome the interfacial tension. When the observing location is shifted to the quarter region, the mid-point between the central line and skin of the specimen, highly elongated LCP lamellae can be observed in Fig. 6b. Eventually, in Fig. 6c, fibrils with high aspect ratios are observed at the skin region, where the greatest shear gradient takes place.

Fig. 7 displays the SEM micrographs of the cryogenically fractured surfaces of the PAr/LCP = 80/20 blends containing various amounts of TGDDM, parallel to the flow direction of the injection-molded specimen and at the skin region. For the uncompatibilized blend, it is observed that the dimensions of the LCP fibrils are relatively larger and irregular as shown in Fig. 7a). The coarse LCP fibrils are improved after adding 0.1 phr TGDDM into the PAr/LCP = 80/20 blend as shown in Fig. 7b). The diameter of the *in situ* fibrils is reduced, indicating that the aspect ratio and the number of the fibrils are increased. A further increase of the TGDDM content results in a greater number and a smaller diameter of the LCP fibrils, as presented in Fig. 7c and 7d). The formation of the *in situ* LCP fibrils in a TP/LCP blend



(A) Core region



(B) Quarter region



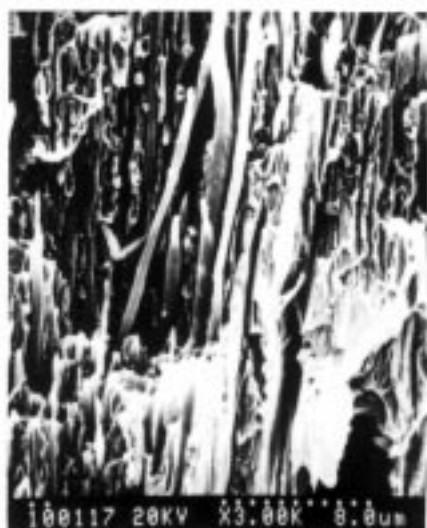
(C) Skin region

Fig. 6. SEM micrographs of the cryogenically fractured surfaces of the PAr/LCP = 80/20 blends, parallel to the flow direction of the injection-molded specimen and at different locations.

can be divided into two steps: The LCP phase is first dispersed into fine droplets, and subsequently the dispersed droplets are elongated into fibrils under high shear rate. Based on Eq. (1), there are three factors that affect the deformation of the LCP phase in the compatibilized PAr/LCP blends: viscosity ratio, shear rate and interfacial tension. The variation of the viscosity ratio arising from the addition of TGDDM itself probably can be ignored because the quantity of TGDDM is small, not higher than 0.5 phr in this study. Moreover, reduced interfacial tension has the similar effect as a higher shear rate that is advantageous to the formation of the LCP fibrils in blends. This TGDDM has been demonstrated as an efficient coupling agent in PAr/LCP blends to produce mixed

copolymers at the interface to lower the interfacial tension. In these compatibilized PAr/LCP blends, the LCP phase has been dispersed into finer droplets than that of the uncompatibilized ones (Fig. 5). Thus, under the same processing conditions, a better-compatibilized blend is expected to possess higher aspect ratio and greater numbers of the LCP fibrils as shown in Fig. 7. Certainly, the reduced initial radius of the LCP phase domain resulting from the reduction of interfacial tension is an important factor to affect the formation of fibrils in compatibilized blends. This effect will be considered next.

The SEM micrographs of the cryogenically fractured surfaces of the PAr/LCP = 95/5 blends containing various amounts of TGDDM, parallel to the flow direction and at



(A) PAr/LCP=80/20



(B) PAr/LCP/TGDDM=80/20/0.1



(C) PAr/LCP/TGDDM=80/20/0.3



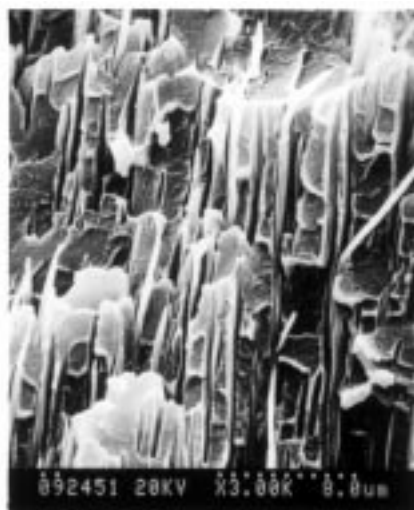
(D) PAr/LCP/TGDDM=80/20/0.5

Fig. 7. SEM micrographs of the cryogenically fractured surfaces of the PAr/LCP = 80/20 blends containing various amounts of TGDDM, parallel to the flow direction of the injection-molded specimen and at the skin region.

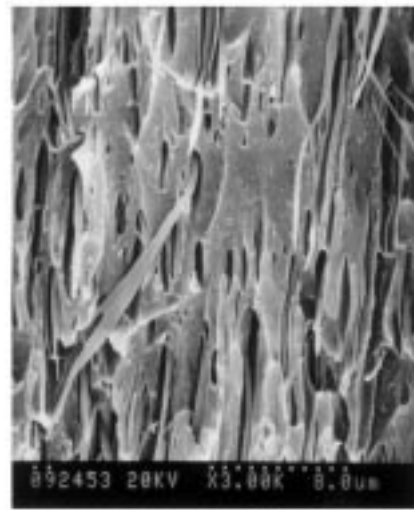


the skin region, are given in Fig. 8. The LCP phase in the uncompatibilized blend is elongated into fibrillar structure as presented in Fig. 8a. In addition, it can be found that the length of the fibrils is somewhat shorter than that in the PAr/LCP = 80/20 blend as comparing Fig. 8a with Fig. 7a. The presence of 0.1 phr TGDDM results in enhancing the formation of a greater number of longer LCP fibrils due to the reduction of the interfacial tension as shown in Fig. 8b. However, a further increase of the TGDDM content (0.3 phr) in the PAr/LCP = 95/5 blend results in finer but shorter LCP fibrils as presented in Fig. 8c. When the blend contains 0.5 phr TGDDM, only ellipsoidal LCP phase domains and a few short and fine fibrils are present as shown in Fig. 8d. The mechanism for the formation of LCP fibrils in PAr/LCP = 80/20 blends can also be applied

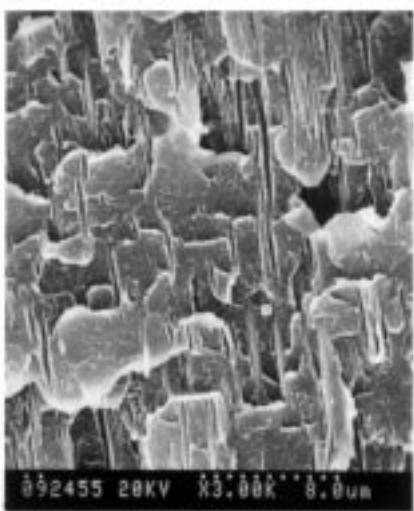
in these PAr/LCP = 95/5 blends, but here the reduced initial radius of the LCP phase domain has to be considered and emphasized. It has been well known that the *in situ* LCP fibrils cannot be created in a blend unless the LCP content exceeding a critical quantity.<sup>[5,39,40]</sup> A smaller LCP content in a TP/LCP blend tends to create a smaller LCP domain size. This implies that a critical LCP domain size is necessary to develop LCP fibrils under high shear during melt processing. If the LCP content is not high enough, the LCP phase will be dispersed into small droplets less than the critical domain size, and then exist as a spherical or elongated structure after shear.<sup>[40]</sup> In these PAr/LCP = 95/5 blends containing various amounts of TGDDM, the interfacial tension decreases progressively with increasing the TGDDM content as would be



(A) PAr/LCP=95/5



(B) PAr/LCP/TGDDM=95/5/0.1



(C) PAr/LCP/TGDDM=95/5/0.3



(D) PAr/LCP/TGDDM=95/5/0.5

Fig. 8. SEM micrographs of the cryogenically fractured surfaces of the PAr/LCP = 95/5 blends containing various amounts of TGDDM, parallel to the flow direction of the injection-molded specimen and at the skin region.

Tab. 2. Tensile and impact properties of PAr/LCP blends.

| Composition               | Tensile  |         |            | Unnotched impact |
|---------------------------|----------|---------|------------|------------------|
|                           | Strength | Modulus | Elongation |                  |
|                           | MPa      | GPa     | %          | J/m              |
| PAr/LCP = 95/5            | 60.4     | 2.06    | 15.6       | 458              |
| PAr/LCP/TGDDM = 95/5/0.1  | 70.4     | 2.19    | 15.9       | 653              |
| PAr/LCP/TGDDM = 95/5/0.3  | 71.0     | 2.13    | 16.4       | 620              |
| PAr/LCP/TGDDM = 95/5/0.5  | 70.5     | 2.11    | 16.2       | 570              |
| PAr/LCP = 90/10           | 74.1     | 2.24    | 12.4       | 424              |
| PAr/LCP/TGDDM = 90/10/0.1 | 80.7     | 2.43    | 13.2       | 550              |
| PAr/LCP/TGDDM = 90/10/0.3 | 81.6     | 2.54    | 13.9       | 582              |
| PAr/LCP/TGDDM = 90/10/0.5 | 82.8     | 2.63    | 14.4       | 596              |
| PAr/LCP = 80/20           | 79.8     | 2.49    | 9.4        | 404              |
| PAr/LCP/TGDDM = 80/20/0.1 | 81.4     | 2.64    | 10.6       | 518              |
| PAr/LCP/TGDDM = 80/20/0.3 | 83.6     | 2.65    | 11.1       | 548              |
| PAr/LCP/TGDDM = 80/20/0.5 | 85.5     | 2.70    | 12.2       | 603              |

expected. Hence, the LCP phase is dispersed into smaller droplets in these compatibilized blends as the result of the reduced interfacial tension. The LCP phase exists as fibrillar structure in PAr/LCP = 95/5 and PAr/LCP/TGDDM = 95/5/0.1 blends as presented in Fig. 8a and 8b respectively. When the concentration of TGDDM is higher than 0.1 phr, the dispersed LCP phase domain size is lower than the critical size to generate LCP fibrils, and consequently the LCP phase domains can only be deformed into short fibrils or even ellipsoids as shown in Fig. 8c and 8d. A similar compatibilization effect on altering the morphology of the LCP fibrils was also observed in our previous studies.<sup>[11, 12]</sup>

*Tensile and impact properties*

The tensile properties and unnotched impact strengths of the PAr/LCP blends for all the compositions in this study are summarized in Tab. 2. For the uncompatibilized PAr/LCP blends, both tensile strength and modulus increase whereas the tensile elongation and impact strength decrease with increasing the LCP content. This is the general trend of mechanical properties for TP/LCP blends when the LCP is the minor component. In the compatibilized PAr/LCP = 80/20 blends, both the tensile properties and impact strength increase substantially with increasing the TGDDM content. The improvement of mechanical properties can be considered in two aspects, strength (tensile strength and modulus) and toughness (tensile elongation and impact strength). Generally, the rod-like molecular conformation and chain stiffness give LCP's excellent "self-reinforcing" properties, which enhance the strength of a TP matrix substantially accompanied by the remarkable decrease in toughness. Therefore, the enhancement on both strength and toughness for the compatibilized PAr/LCP = 80/20 blends is quite unusual, and only a few

similar cases have been reported before.<sup>[12-14]</sup> The reduction of the interfacial tension arising from the improved compatibility by the addition of TGDDM results in greater numbers of LCP fibrils with higher aspect ratios and consequently a higher strength of the PAr/LCP = 80/20 blends after compatibilization. The improved compatibility also leads to the enhancement of interfacial adhesion between phases, so the fracture energy can be transferred more efficiently under loading to increase the toughness. By contrast, the enhancement of tensile and impact properties for the compatibilized PAr/LCP = 95/5 blends with the increase of TGDDM content is not so evident as in the other two series as listed in Tab. 2. The tensile modulus and impact energy of the compatibilized PAr/LCP = 95/5 blends tend to decrease with increasing the TGDDM content when the concentration of TGDDM is higher than 0.1 phr. This phenomenon can be correlated well with the corresponding morphologies. The LCP phase can not be elongated into desired longer fibrillar structure in the PAr/LCP = 95/5 blends containing higher TGDDM content as shown in Fig. 8, and thus the anticipated self-reinforcing properties cannot be achieved. Nonetheless, the overall mechanical properties are still improved after compatibilization, even though the effect of self-reinforcement on enhancing the mechanical properties of the PAr/LCP = 95/5 blends with high TGDDM content is not achieved. The results in mechanical properties and morphologies illustrate that the generation of LCP fibrils with high aspect ratio and improvement of interfacial adhesion are the two hinges to enhance the performance of the compatibilized PAr/LCP blends.

**Conclusion**

The tetrafunctional epoxy resin, tetraglycidyl-4',4'-diaminodiphenyl methane (TGDDM), has been demonstrated

to be an efficient reactive compatibilizer for the PAr/LCP blends in this study. TGDDM has the chance to react with PAr and LCP at the interface simultaneously to produce the PAr-co-TGDDM-co-LCP mixed copolymers during melt blending, and these interfacially formed copolymers tend to anchor along the interface preferentially to serve as effective compatibilizers for PAr/LCP blends. Potential reactions between PAr, LCP, and TGDDM during melt mixing are confirmed qualitatively by means of torque measurement. The *in situ*-formed compatibilizer distributed at the interface is able to reduce the interfacial tension and enhance the interfacial friction in the melt and the interfacial adhesion in the solid state. SEM morphologies show that the dimensions of the dispersed LCP phase domains have been reduced obviously in the compatibilized PAr/LCP blends. The reduced interfacial tension makes the LCP phase disperse into fine droplets first in the compatibilized blends, and then facilitates the dispersed LCP droplets into elongated fibrils with high aspect ratios during the injection-molding process. The TGDDM content affects the deformation of the LCP fibrils in the compatibilized PAr/LCP blends. For the blends containing adequate amounts of LCP (>10%), the LCP phase tends to deform into greater numbers and finer fibrils after compatibilization. For low LCP content blend (PAr/LCP = 95/5) with high TGDDM content (0.3 phr or higher), the LCP phase can only be deformed into fine and short fibrils or even ellipsoids because the LCP domain size has been reduced to be less than the critical size required for fibril formation. The overall mechanical properties of the PAr/LCP blends are substantially improved after compatibilization by this coupling type reactive compatibilizer. The formation of greater numbers of finer LCP fibrils and improved interfacial adhesion of the compatibilized PAr/LCP blends relative to those uncompatibilized ones are the two most important factors to enhance the mechanical properties of PAr/LCP blends.

*Acknowledgement:* This research is financially supported by the Chinese Petroleum Corporation, Taiwan, ROC, under Contract No. 87-CPC-E-009-006.

Received: September 13, 1999

Revised: January 13, 2000

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