Blends of amide modified polybutylene terephthalate and polycarbonate: phase separation and morphology

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Blends are made of polycarbonate (PC) and poly(butylene terephthalate) (PBT) or amide modified poly(butylene terephthalate) (PBTA). The blends were prepared by melt blending. The blend morphology was studied by transmission electron microscopy. The PC phase was stained with RuO4. The particle sizes in the PC/PBT blends are small (less than 0.5 μm) and the particle sizes in the PC/PBTA blends are larger (0.5–5 μm). The blends were stabilized against transesterification by inactivation of the titanate catalyst in the PBT/PBTA with triphenyl phosphite (TPPi). A side effect of TPPi is that it acts as a plasticizer for the PC phase. The results were corrected for this effect. Also studied are the influence of the amide concentration in the PBTA from 0% (PBT) to 25 mol% (PBTA25) and the concentration of PBT(A) in the PC/PBT(A) blend over the whole composition range on the glass transition temperature (Tg) of the PC phase of the blend. Also studied are the crystallization behaviour as function of PC/PBT(A) composition and the phase separation on annealing. The PC/PBT blends were found to be partially miscible. As a result of this, the Tg of the PC was lowered and the crystallization of PBT slowed down. The PC/PBTA blends with 20–25 mol% amides in the PBTA were immiscible. The crystallization rate of the PBTA was high, and was not affected by the presence of the PC. The blends with PBTA had a higher melting temperature, were faster crystallizing, and had a higher Tg of the PC phase. © 1997 Elsevier Science Ltd.

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INTRODUCTION

It is well-known for polymer blends that the apparent properties and morphology do often not reflect an equilibrium situation. In blends of an amorphous polymer and a semi-crystalline polymer, the phase behaviour is strongly dependent on blending and cooling conditions. In the case of partial or complete miscibility of the components in the molten state, the cooling rate and the kinetics of non-isothermal crystallization will influence the final extent of phase separation at room temperature.

Miscibility of polycarbonate/poly(butylene terephthalate)

Blends of polycarbonate (PC) and poly(butylene terephthalate) (PBT) represent a perfect example of the complex interplay between phase separation and crystallization. Several authors have reported that PC/PBT, after melt blending with inhibition of transesterification, is partially miscible1–4. Most articles, however, do not comment on the miscibility of PC and PBT in the melt. Singh5 observed a large decrease of melt flow index of PC, when only 5–10 wt% of PBT was added. This indicates some solubility of PBT in PC. Hobbs et al.3 and Delimoy et al.6 observed the presence of PC in the interlamellar zones of PBT. From this they concluded that in the molten state PC and PBT must have been partially miscible, but on cooling, phase separation and crystallization of PBT is taking place. With the dispersed blends one can have the case with a PBT rich continuous phase (Figure 1a) and with a PC rich continuous phase (Figure 1b).

The solubility of PBT in PC in the solid state is rather low, and in principle not dependent on the blend composition (lever rule of a phase diagram). The quoted decreasing glass transition temperature (Tg) of PC with increasing PBT content concerns non-stabilized blends1,2,7. In PC/PBT blends, stabilized with 0.5 wt% triphenyl phosphite (TPPi), a decrease of the Tg was observed from 147°C (pure PC) to a level of 130–135°C8.
Table 1 Properties of PC, PBT and PBTA

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Trade name</th>
<th>$M_w$ (g mol$^{-1}$)</th>
<th>$\eta_{inh}$ (dL g$^{-1}$)</th>
<th>$T_m^a$ (°C)</th>
<th>$\Delta H_m$ (J g$^{-1}$)</th>
<th>$T_g^b$ (°C, d.s.c.)</th>
<th>$T_g^c$ (°C, d.m.a.)</th>
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</thead>
<tbody>
<tr>
<td>PC</td>
<td>Lexan 125</td>
<td>23.000</td>
<td>0.50</td>
<td>145</td>
<td>144</td>
<td>52</td>
<td></td>
</tr>
<tr>
<td>PC</td>
<td>Lexan 145</td>
<td>26.000</td>
<td>0.54</td>
<td>147</td>
<td>145</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td>PBT</td>
<td>Valox 315</td>
<td>105.000</td>
<td>1.23</td>
<td>212 + 220</td>
<td>42</td>
<td>29</td>
<td></td>
</tr>
<tr>
<td>PBT-2</td>
<td></td>
<td>1.39</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PBT A10</td>
<td></td>
<td>2.12</td>
<td></td>
<td>201 + 229</td>
<td>62</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PBTA20-52A</td>
<td></td>
<td>1.08</td>
<td></td>
<td>224 + 252</td>
<td>20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PBTA25-2A</td>
<td></td>
<td>0.96</td>
<td></td>
<td>263</td>
<td>28</td>
<td>75</td>
<td></td>
</tr>
</tbody>
</table>

*a* $T_m$ from second heating scan. The main melting peak is underlined

*b* $T_g$ from second heating scan with d.s.c.

*c* $T_g$ from first heating scan with d.m.a.

Hobbs et al.\(^3\) give as a possible second reason for this strong lowering of the $T_g$ the plasticizing effect of the stabilizer.

Bertilsson and coworkers\(^9,10\) observed that the phase separation in PC/PBT blends increased by annealing at temperatures close to or above the $T_g$ of PC. Delimoy et al.\(^6\) reported that during annealing at 220°C the PBT lamellae were growing from the interface, inside the PC-rich phase, depleting the latter from dissolved PBT. Apparently, the extent of PBT crystallization also influences its solubility in a PC blend.

### Non-isothermal crystallization

PBT and PC are, in the melt, partially miscible. The PBT crystallization from the melt with the high $T_g$ PC depends strongly on the crystallization window and the cooling rate. The ‘crystallization window’ of the blend is determined by the melting temperature ($T_m$) and the glass transition of the phase upon cooling ($T_g$). The crystallization rate is at its maximum at $T_c$. This crystallization temperature ($T_c$) of PBT is strongly dependent on the cooling rate\(^11\). The $T_g$s of PBT and PC are a little dependent on the cooling rate.

The rate of crystallization from an immiscible blend is hardly affected by the second phase. The crystallization of PBT in a partially miscible PC blend can occur from a PBT-rich phase or from a PC-rich phase. The crystallization from the PBT-rich phase will be hindered by the presence of dissolved PC with a higher $T_g$. The chain mobility is reduced, and with that the crystallization rate slowed down. The rate of PBT crystallization from the PC-rich phase is strongly hindered by the high $T_g$ of the phase. The crystallization window is here small, and the rate of crystallization very slow.

The crystallization of PBT from PC/PBT blends at low cooling rates ($<5°C \text{ min}^{-1}$) was found to be independent of the PC content\(^12\). At higher cooling rates of blends with a high PC concentration (e.g. 60/40 wt% blends) (Figure 1b) the PBT appeared to crystallize in steps\(^8,12\). With a cooling rate of 10°C min$^{-1}$ the first exotherm is at 187°C and the second at 205°C. This second exotherm is below the $T_g$ of the PC phase. This double crystallization behaviour was ascribed to a crystallization of PBT from the different phases. For an 80/20 wt% PC/PBT blend one crystallization exotherm below the $T_g$ of PC (at 102°C) was observed. The PBT rich phase is here a finely dispersed phase. The particles are small compared to the spherulite size in the homopolymer, and thus the nucleation might have been a problem.

Blends of polycarbonate with polyesteramides (PBTA) can be obtained in a similar way to PC/PBT blends\(^14\). The diamine units in the PBTA are expected to change the miscibility with PC. The solubility parameter $\delta$ for PC and PBT is about 21 and 22 MPa$^{1/2}$ respectively, and by the incorporation of diamide units in PBTA the difference $\Delta \delta$ increases\(^15\). As a result of this, the miscibility of PBTA with PC will be less and the $T_g$ of the PC phase less affected by the presence of the PBTA. The transesterification between the PC and the PBT/PBTA which is catalysed by titanate residues in the PBTA can be suppressed by addition of TPPi. A side-effect of TPPi is that it plasticizes the PC\(^14\).

We studied the phase behaviour, the phase structure and the crystallization of these new PC/PBTA blends. The results of these PC/PBTA blends were compared with those of PC/PBT blends.

### EXPERIMENTAL

#### Materials

PC (Lexan 145 and 125) and PBT (Valox 315) were kindly supplied by GE Plastics (Bergen op Zoom). Lexan 145 was used unless otherwise stated. The synthesis of PBT-2 and PBTA10-52A, PBTA20-52A and PBTA25-2A have been described\(^11\). Their properties are given in Table 1. TPPi was purchased from Aldrich (density 1.19 g cm$^{-3}$, purity >97%) and used as received. The blend components were dried at 100°C in vacuo overnight before blending and testing.

![Figure 2](https://example.com/figure2.png)
Amide modified PBTA and PC blends: A. C. M. van Bennekom et al.

PC/PBT

90/10

70/30

50/50

30/70

10/90

PC/PBTA
Amide modified PBTA and PC blends: A. C. M. van Bennekom et al.

**Blending method**

PC Lexan 145 and PBTAxx were melt blended in a DSM mini-extruder at 270°C and 30 rpm\(^1\). The TPPi addition was \(16 \times \text{TPPi}/\text{Ti (mol/mol)}\). PC Lexan 125 and PBT Valox 315 were melt blended with 0.5 wt% TPPi in a Berstorff DSE at 255°C, 60 rpm and a throughput of 2 kg h\(^{-1}\).

**Compression moulding**

Torsion test bars were prepared on a Lauffer OPS 40 press at 20°C above the melting temperature. During 3–1–3 min a pressure of 0–3–10 bar respectively was applied. The mould was cooled (about 10°C min\(^{-1}\)) and the specimen was released.

**Differential scanning calorimetry**

A Perkin Elmer DSC7 equipped with a PE-7700 computer and TAS-7 software was used to study the melting and crystallization transitions. The heating rate was 20°C min\(^{-1}\) and the cooling rate was varied from 10 to 160°C min\(^{-1}\). The peak maximum was taken as transition temperature \(T_m\) or \(T_c\). The \(T_g\) was defined from the second heating scan, as the temperature half way up the heat capacity jump. The sample size was 10–12 mg. Tin was used as the calibration standard.

**Differential mechanical analysis**

Differential mechanical analysis (d.m.a.) was performed with a Myrenne ATM3 torsion pendulum at 1 Hz with a heating rate of 1°C min\(^{-1}\). The loss modulus \(G''\) was recorded as function of temperature, with the maximum of \(G''\) taken as the glass transition. The torsion bars (about 70 mm × 9 mm × 2 mm) were dried at 100°C in vacuo overnight before analysis.

**Electron microscopy**

Morphology studies of cross sections of extruded strands were performed using a CM2 Philips transmission electron microscope (TEM). Thin sections (\(\sim 0.1 \mu m\)) were microtomed (at \(-50°C\)) and stained with ruthenium tetroxide (RuO\(_4\)) to enhance the contrast between the phase\(^6,16\). Scanning electron microscopic (SEM) analysis was carried out on extrudate broken in liquid \(N_2\), using a Hitachi SEM Model S-800 (7 keV).

**RESULTS AND DISCUSSION**

**Morphology of the blends**

The morphology of the extrudates was studied with TEM, with varying blend ratios (Figure 2). Due to preferential staining of the PC phase, this phase appears black in the TEM photographs. It is clear that these blends have a biphasic structure and range from a continuous PC-phase to a continuous PBT/PBTA phase.

**90/10 wt% blends** (Figures 2a and 2b). For the PC/PBT blend the particles are well dispersed, and their size is in the range of 0.1–0.2 μm. The particle sizes for the PC/PBTA blend were in the range of 0.1–0.5 μm.

**70/30 wt% blends** (Figures 2c and 2d). For PC/PBT the average particle size was about 0.1–0.3 μm. The degree of dispersion did not decrease significantly by using a higher screw speed, 100 instead of 30 rpm. The particle size of the PBTA phase in PC was larger (0.5–1.0 μm). By application of a higher shear (100 rpm extrusion) the particles became less spherical and decreased in size to about 0.6 μm.

**50/50 wt% blends** (Figures 2e and 2f). At this intermediate blend ratio PC/PBT and PC/PBTA20 have a co-continuous morphology. The thickness of the co-mingling strings was about 0.2–0.4 μm in PC/PBT, whereas the thickness was about 1–2 μm in PC/PBTA20.

**30/70 wt% blends** (Figures 2g and 2h). PC/PBT contains a dispersed PC phase with a size of about 0.2–0.5 μm, which is somewhat larger than the PBT particle size at a 70/30 wt% ratio (Figure 2e vs Figure 2a). This can be ascribed to the high melt viscosity of PC.

![Graph](https://via.placeholder.com/150)

**Figure 3** Glass transition of the PC-phase in PC/PBTA (70/30 wt%) vs amide content in PBTA: □, 30 rpm; ○, 100 rpm
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Amide modified PBTA and PC blends. A. C. M. van Bennekom et al.

PC/PBTA20 (30/70 wt%) in Figure 2h shows a particle size of 2–5 μm, which indicates that PBTA20 is less compatible with PC than PBT.

10/90 wt% blends (Figures 2i and 2j). The particle sizes of the PC/PBT blends are in the range of 0.1–0.2 μm. This is comparable to the 90/10 wt% blend. The particle size of the PC/PBTA blends are much larger and in the range of 0.2–1.0 μm.

From these TEM studies it is clear that the PBTA blends have larger particle sizes than the PBT blends. This means that with PBTA the interfacial tension with PC is increased. This increase is due to the incorporation of diamide units.

Amide content in PBTA

The extent of miscibility of PBTA in the PC phase has been derived from the shift in the T<sub>g</sub> of the PC phase (T<sub>g</sub> PC) of a 70/30 blend. The blends had been stabilized with TPE and had a very low (<0.2 mol%) degree of transesterification after extrusion. With increasing amide content in the PBTA the T<sub>g</sub> of the PC phase in PC/PBTA blends (70/30 wt%) increased (Figure 3). The PC T<sub>g</sub> of the blends made at a higher screw speed (100 vs 30 rpm), was at a lower temperature. More intense
mixing resulted in a higher miscibility. In these reactive blends is the creation of a larger interphase a first step in increasing miscibility.

The $T_g$ of neat PC (Lexan 145) was located at 147°C. The $T_g$ of PC with TPPi is, however, lower. For the used amounts of TPPi in the blends this $T_g$ is expected at a temperature 10°C lower. The $T_g$ of PC/PBT is lower than that of the PC (with TPPi). So some PBT seem to have dissolved in PC. With increasing amide content the $T_g$ of the PC increases, and in the 20–25% amide blends the $T_g$s are comparable to the $T_g$ of the PC (with TPPi). Thus without transesterification no PBTA20 seem to have dissolved in the PC. These data also indicate that the $T_g$s of these PC blends can be further increased if less titanate stabilizer is added, under the condition that still no transesterification is taking place.

### Blend ratio

The effect of the blend composition on the $T_g$-shift has been studied over the whole concentration range (Figure 4). The $T_g$s were corrected for the amount of TPPi added to the system. Of the 10/90 blends no $T_g$ of the PC phase could be observed.

With increasing PBT content the PC $T_g$ is lowered. A maximum lowering of 13°C was observed. This suggests an increase in the amount of dissolved PBT with concentration. With the Fox relationship this 13°C lowering means that 13% PBT is dissolved in the PC phase. The blends with PBTA20 show no change in PC $T_g$ with composition. Thus, over the whole studied range the PBTA20 and the PC seem to be non-miscible.

### Melting temperature

The melting temperature in a partially miscible blend can be depressed. This melting point depression in a miscible blend depends on the concentration of the dissolved polymer and the polymer–polymer interaction parameter. In Figure 5, the melting temperatures of PC/PBT and PC/PBTA20 melt blends are presented as a function of their blend ratio.

The melting temperatures of the used neat polymers PBT and PBTA20 are 220 and 252°C respectively. In PC/PBT, the melting temperature of PBT decreased slightly with increasing PC content and some broadening of the melting peak at a low PBT content was observed. Radusch et al.17, however, found a strong broadening of the melting transition of PBT with only a small addition of PC, and ascribed this to the partial miscibility of PC/PBT. In PC/PBTA20 blends, the melting temperature remained virtually unchanged. A further broadening of the PBTA20 melting peaks did not occur which indicates the absence of PC in interlamellar zones of the PBTA spherulites.

### Crystallization

In the PC/PBT blends cooled at 20°C min^{-1} the PBT crystallization temperature ($T_c$) decreases with PC content (Figure 6). This decrease is strong in the PBT dispersed blends. The crystallization of PBT is probably only from the PBT rich phase as the PC rich phase has a very high viscosity. The PBT rich phase is at 70/30 and 90/10 composition the dispersed phase with a particle size of about 0.1–0.4 μm (Figure 2). In these particles are smaller than regular PBT-spherulites (1–20 μm)18 and the nucleation rate in these small particles might be too slow.8,12

The crystallization temperature of the dispersed PBTA20 in PC/PBTA blends minimal hindered by PC and it crystallizes as fast as the neat polymer. The faster crystallization behaviour of dispersed PBTA20 compared to PBT is possibly due to:

- a larger crystallization window ($T_m - T_g$);
- a higher rate of crystallization;
- a larger domain size;
- less dissolved PC in the PBTA phase.

At cooling rates above 40°C min^{-1} the 90/10 PC/PBT blend did not crystallize any more. Injection moulded PC/PBT (70/30 wt%) samples were nearly transparent, suggesting that under those conditions crystallization...
Table 2  Effect of annealing on the $T_g$s of PC/PBT and PC/PBTA20 (d.m.a., 1°C min$^{-1}$)

<table>
<thead>
<tr>
<th></th>
<th>PC (Lexan 125)</th>
<th>PBT (Valox 315)</th>
<th>PC/PBT + TPPI (30/70 wt%)</th>
<th>PBTA20prec. (no TPPI)</th>
<th>PC/PBTA20prec. (70/30 wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>After moulding</td>
<td>144</td>
<td>52</td>
<td>60 + 133</td>
<td>66$^a$</td>
<td>68 + 140</td>
</tr>
<tr>
<td>22 hrs 140°C</td>
<td>–</td>
<td>–</td>
<td>55 + 146</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>20 hrs 180°C</td>
<td>–</td>
<td>–</td>
<td>52 + 150</td>
<td>–</td>
<td>72 + 140 (broad)</td>
</tr>
</tbody>
</table>

$^a$ Ref. 11

Figure 7  Influence of annealing on loss modulus ($G''$) of PC/PBT (30/70 wt%) melt blend of Lexan 125 and Valox 315 with 0.5 wt% TPPI: --, after compression moulding; --, after 20 h at 180°C, N$_2$

Figure 8  Influence of annealing on loss modulus ($G''$) of PC/PBTA20prec. (70/30 wt%) melt blend of Lexan 125 and precipitated PEA20: --, after compression moulding; --, after 20 h at 180°C, N$_2$
Figure 9 SEM photographs of fracture surfaces of PC/PBTA20 (70/30 wt%) perpendicular to the extrusion axis: (a) directly after extrusion; (b) after annealing (20h at 180°C, N2)

during the cooling cycle was severely hindered. On reheating these materials crystallized.

At very high cooling rates, as with injection moulding, PBTA in PC/PBTA still crystallized. The PBTA in the blends is not only crystallizing faster, but also the secondary crystallization will be less.

Phase separation upon annealing

When crystallizable polymers are maintained at a temperature close to their melting temperature, the crystallinity increases considerably. Annealing of partially miscible blends can promote phase separation induced by crystallization.

The effect of annealing on PC/PBT and PC/PBTA20 blends is presented in Table 2. We have used a commercial PBT (Valox 315) with 0.5 wt% TPPi, and a solution of precipitated PBTA20 (PBTA20prec.14) in order to minimize the chance of interchange reactions.

Although PC/PBTA20prec. was melt blended without TPPi, the transreactions appeared to be suppressed by the precipitation method14. Both melt blends were compression moulded into torsion bars and annealed in an oven with N2 flow. Before and after annealing the loss modulus G" vs temperature was recorded by d.m.a. (Figures 7 and 8). The PC/PBT melt blend appeared directly after compression moulding (slowly cooled from the melt) to be partially miscible. The torsion curves contained two maxima of the G" at temperatures between the Tg of PBT and PC (Figure 7). Upon annealing for 22 h at 140°C (close to the Tg of PC) the glass transitions shifted towards the homopolymers and the G" peaks became less broad. This is in agreement with the observed increase of phase separation after ageing, as reported by Bertillon et al.9. An even higher degree of phase separation could be achieved in the case of annealing of the blend for 20 h at 180°C. The observed miscibility of the unannealed sample between PC and PBT seems to have disappeared. The Tg of PC phase is even higher than that of the starting PC (Lexan 125). Surprising is that the earlier observed solvent effect of TPPi seems to have disappeared14. Possibly the TPPi has phase separated too.

The PC/PBTA20prec. blend appeared already highly phase separated after melt blending and compression moulding (Figure 8). Annealing at 180°C did not lead to a significant further increase of phase separation. The small increase of the Tg of PBTA20 can be attributed to an increased densification and an increased restriction of the chain mobility. The location of the glass transition of the PC-phase remained unchanged. The broadening of the PC-peak after 20 h annealing at 180°C was assigned to the occurrence of PC crystallization. Of the annealed samples, the morphology was studied with SEM (Figure 9). The change in morphology of PC/PBTA20prec. (without TPPi) upon annealing for 20 h at 180°C was significant. The fracture surface of PC/PBTA20 extrudate directly after extrusion (Figure 9a) has been compared with the fracture surface of extrudate after the mentioned anneal treatment (Figure 9b). The SEM-photograph in Figure 9a indicates that the interfacial strength of the interface directly after extrusion was very low. After annealing of the extrudate at 180°C, the
interfacial region became more diffuse (Figure 9b). Probably, some PC trapped in the PBTA phase has diffused out, and/or some mixing of PBTA and PC in the interlayer has occurred. The dispersed PBTA20-phase showed an improved adhesion with the PC matrix.

CONCLUSIONS

The phase behaviour of PC/PBT and PC/PBTA20 melt blends has been compared. Upon cooling two processes, liquid–liquid demixing and crystallization, occur simultaneously. With increasing amide content in PBTA the T_g of PC showed a smaller reduction in the glass transition. If this glass transition is corrected for the presence of TPPi there is some T_g lowering for the PBT blends and none for the PBTA20 blends. The PC/PBTA20 blend and the PC/PBTA25 blend seem to be fully phase separated.

The morphology of PC/PBT and PC/PBTA20 extrudates with varying composition as studied by TEM showed that the structures are biphasic and range from a continuous PC phase to a continuous PBTA phase. In the intermediate composition range a co-continuous blend structure was observed. The morphology of PC/PBTA20 was in general more coarse than that of PC/PBT.

The crystallization of PBT in PC-rich blends was, at low PBT concentrations, significantly reduced. On reheating the PC/PBT blends showed a high degree of secondary crystallization. The crystallization temperature of PBTA20 in PC/PBTA20 blends was not affected by the presence of the PC.

For the faster crystallization of the PBTA systems several possible reasons can be given: the melting temperature of PBTA is higher and therefore the crystallization window larger, the faster the crystallization behaviour of PBTA, the larger particle size of the PBTA phase which makes the system less critical for the nucleation density and the better phase separation of the system.

On annealing the PC/PBT blend the glass transitions shifted towards the homopolymers and the earlier observed partial miscibility seems to have disappeared. The miscibility of PBTA in PC in the fast cooled blends seem to be due to a slow demixing process. As the T_g of the PC phase of the annealed blend is at 150°C it is not clear what happened to the plasticizing effect of the added TPPi. Possibly the TPPi has phase separated too. The PC/PBTA20 blend, prepared from Lexan 125 with solution precipitated PBTA20 (no TPPi), was already highly phase separated before annealing, and upon annealing no shift in T_g was observed. SEM photographs showed that the annealing procedure had improved the interfacial bonding of PC/PBTA20 extrudates significantly.

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