PII: S0032-3861(96)00866-X

*Polymer* Vol. 38 No. 12, pp. 3017–3024, 1997
© 1997 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0032-3861/97/$17.00 + 0.00

# Blends of amide modified polybutylene terephthalate and polycarbonate: transesterification and degradation

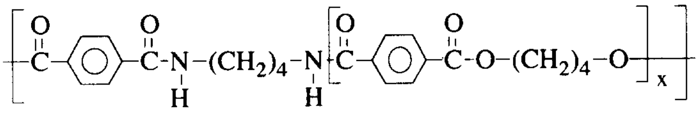
**A. C. M. van Bennekom*, D. T. Pluimers, J. Bussink† and R. J. Gaymans‡**
*University of Twente, PO Box 217, 7500 AE Enschede, The Netherlands*
*(Received 16 August 1996)*

Blends were made of polycarbonate (PC) and polybutylene terephthalate (PBT) or amide modified polybutylene terephthalate (PBTA). The blends were prepared by solution casting, solution precipitation and melt mixing. The transesterification interchange reactions were followed by $^1$H n.m.r. analysis. The change in the glass transition temperature ($T_g$) of PC has been studied as function of blending conditions, the addition of titanate catalyst inactivator, the content of Li-residues and the molecular weight of the polymers. A correlation is made between the degree of transesterification and the lowering of the glass transition. Triphenyl phosphite (TPPi) (0–2.2 wt%) was used as titanate catalyst inactivator. TPPi was found to be an effective catalyst inactivator however, this low molecular weight compound has also a strong plasticizing effect on PC. A concentration of 0.5 wt% TPPi gave a good stabilization against transesterification. Without transesterification the PBTA was found to be less miscible with PC than PBT and the PC/PBTA blends had higher $T_g$s for the PC phase than PC/PBT and a higher melting temperature of the system. © 1997 Elsevier Science Ltd.

**(Keywords: polycarbonate; polybutylene terephthalate; polyesteramide)**

## INTRODUCTION

The properties of a polymer blend depend on its morphology and for a fine phase structure some miscibility is required. If chemical reactions take place during blending, the miscibility increases and a finer phase structure can be obtained. If considerable chemical reactions between the polymers take place a completely miscible system is obtained. Blends of polycarbonate (PC) and polybutylene terephthalate (PBT) are slightly miscible but as interchain reactions between the carbonate and the ester are possible, completely miscible systems can also be obtained. A large amount of research on PC/PBT blends has been focused on the interchange and degradation reactions[1–4]. Deveaux *et al.*[1] reported for PC/PBT that with increasing time and temperature a blend of homopolymers changed into a mixture of block-copolymers and finally into completely randomized copolymers. In the presence of a titanate catalyst, transesterification appeared to be the only significant reaction[1]. Titanate is present in the PBT as it is the catalyst for the polymerization of PBT.



(1)

PBTA

A way to influence the amount of interchange reactions is to change the miscibility of PBT/PC. PBT can be modified with the bisesterdiamide of butanediamine and dimethyl terephthalate to the amide modified PBT (PBTA)[5,6].

PBTA has a higher melting and glass transition temperature than PBT[6,7]. Also the crystallization rate is higher and the solvent resistance better. PC/PBTA blends have yet to be reported.

Interchange reactions of PC with polyamides may occur, as carbonate groups are very sensitive to basic (alkaline) compounds[8]. Direct interchange of polyamide with polycarbonate has not yet been reported. However, titanate might catalyse the interchange of carbonate groups with amide groups, resulting in ester and urethane linkages.

### *Inactivation of titanate catalyst*

The transesterification reactions can be suppressed by inactivation of the titanate catalyst, residing in PBT (and PBTA) after polymerization. Deveaux[2] observed that phosphites, such as di-n-octadecyl phosphite (DOPi) diphenyl phosphite (DPPi) and triphenyl phosphite

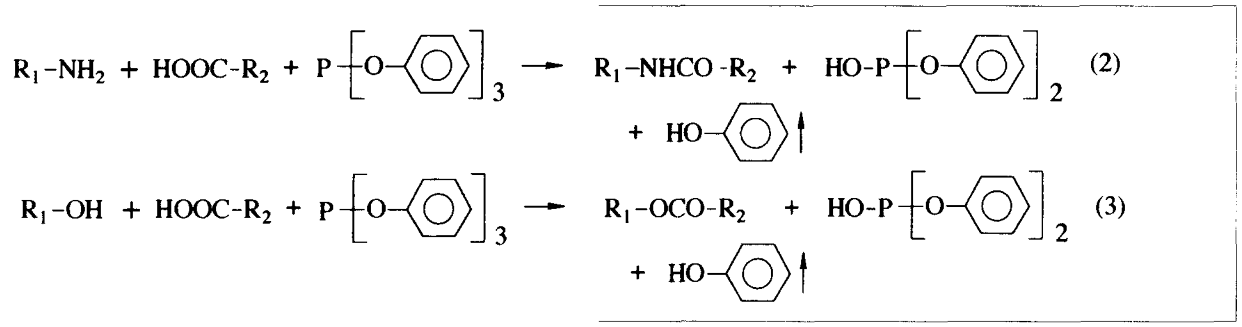
---

* Present address GE Plastics, PO Box 117, 4600 AC Bergen op Zoom, The Netherlands

† Franselei 27, Kapellen, België

‡To whom correspondence should be addressed

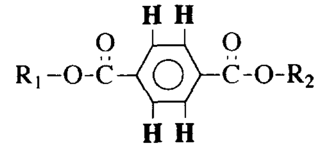
(TPPi), were very effective in the inactivation of $Ti(OR)_4$ compounds. Delimoy[9] reported that the use of DOPi and DPPi in PC/PBT blends also resulted in degradation of the blend, as the compounds contained water and alcohol impurities. On the other hand, TPPi appeared to be only active as inhibitor after an exchange of its phenol ligand, e.g. by hydrolysis. TPPi has also been applied as a chain extender of polyesters and polyamides. Aharoni[10,11] proposed mechanisms for the amidation of amino and carboxylic acid endgroups (**2**) and for the esterification of hydroxyl and carboxylic acid endgroups (**3**). Delimoy[9] measured a chain extending effect of TPPi on PBT, present in a PC-blend. In these reactions DPPi and phenol are released. It was expected that DPPi instead of TPPi is the actual inhibitor of titanate compounds in PBT[9].


(2)

(3)

However, hydrolysis of TPPi leads to DPPi without increasing the molecular weight of the polymer. With further hydrolysis of DPPi, phosphoric acid $P(OH)_3$ will be formed. The acid can tautomerize in phosphonic acid $P(O)(H)(OH)_2$. The latter is a possible titanate inhibitor according to Verhoeven[12].

Bis(2,4-di-t-butylphenyl)pentaerythritol diphosphite (Ultranox 624 of Borg Warner Chemicals) was reported only to be effective in the suppression of transesterification after hydrolysis to phosphonates[13]. Phosphoric acid[12] and sulfuric acids[14] and their salts have also been mentioned as inhibitors. Ciba Geigy[15] even patented the suppression of tranesterification in PC/PBT melt blends by addition of about 1 wt% of polyamide (a 'CONH-containing polymer'), e.g. Nylon-6.


(4a)

In this study TPPi has been used as an inhibitor of titanate compounds. Despite the release of phenol during processing it has the advantage of easy addition, being a liquid up to 180°C. TPPi is also known for its melt stabilization of PBT and PET, the prevention of colour formation[16–18] and the decomposition of hydroperoxides which might be present in the polymer.

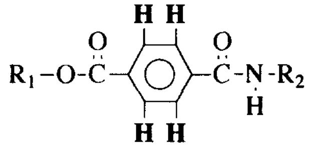
### *Identification of interchange reactions*

The extent of interchange reactions in PC/PBT and PC/PBTA blends can be determined by structure analysis. We have studied the change in polymer structures mainly by $^1H$ n.m.r. The degree of transesterification was calculated by the method of triad analysis, reported by Deveaux *et al.*[19]. The calculation was based on a change upon reaction, of the chemical shift $\delta$ of terephthalic protons in the triads. Several types of terephthalic triad sequences are possible depending on the neighbouring groups (R), butylene and/or bisphenol-A (*Table 1*). In the case of an ester–ester triad (**4a**), code $3^{EE}$ indicates a PBT-sequence and $3^{E^*E}$ or $3^{E^*E^*}$ indicate that one or two transesterification reactions have taken place. In the case of an ester–amide triad (**4b**), code $3^{EA}$ corresponds to a double doublet of a T4T sequence. The triad $3^{E^*A}$, transesterified on one side, has not been observed in the $^1H$ n.m.r. scan due to the low amide concentration used in PBTA and overlap of peaks. The chemical shift of the $3^{E^*A}$ triad has been estimated by means of the change in $\delta$ from $3^{EE}$ to $3^{E^*E}$.

**Table 1** Characteristic $^1H$ chemical shifts for terephthalic triads in PC/PBTA copolymers

| Triad | $R_1$ | $R_2$ | $\delta$ (ppm) | | |
|---|---|---|---|---|---|
| $3^{EE}$ | butylene | bytylene | 8.17 | *s* | (3a) |
| $3^{E^*E}$ | bisphenol-A | butylene | 8.20–8.36 | *q* | (3a) |
| $3^{E^*E^*}$ | bisphenol-A | bisphenol-A | 8.40 | *s* | (3a) |
| $3^{EA}$ | butylene | butylene | 7.85 ± 8.17 | *dd* | (3b) |
| $3^{E^*A}$ | bisphenol-A | butylene | 7.89 ± 8.37[a] | *q* | (3b) |

[a] Expected, not observed


(4b)

The degree of transesterification, or the degree of randomization ($r$), was defined as the mol ratio of new bisphenol-A terephthalic ester linkages to the total amount of terephthalate ester linkages.

$$r = \frac{2\cdot 3^{E^*E^*} + 3^{E^*E} + 3^{E^*A}}{2\cdot(3^{EE} + 3^{E^*E^*} + 3^{E^*E}) + (3^{E^*A} + 3^{EA})}\cdot 100\%\ \text{[mol\%]} \tag{1}$$

The detection limit for the determination of $r$ was about 0.2 mol%. For equation (1) it was assumed that ester–amide and carbonate–amide interchange reactions can be neglected. It has been shown that the extent of ester–amide interchange in PBTA20 after 1 h at 270°C was relatively low[20].

The amide content ($X_A$-NMR $2^A$) in PBTA was calculated as a mol fraction of amide methylene sequences, $2^A/(2^A + 2^E)$. With a high degree of degradation reactions, a new $2^{A'}$ peak appeared (*Figure 1*) which

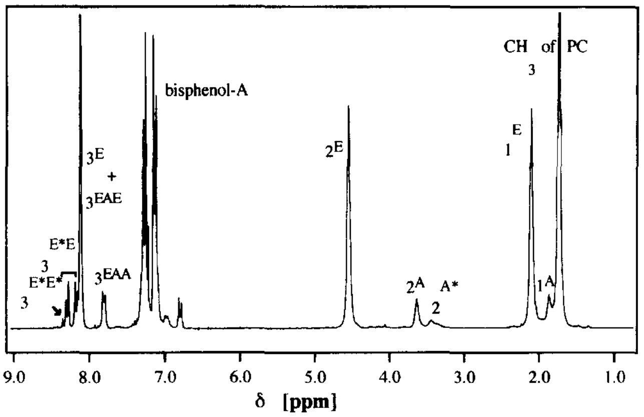


**Figure 1** Example of a $^1$H n.m.r. scan of PC/PBTA20 with a degree of transesterification (*r*) of 11.4 mol% and a terephthalic amide content $X_A$ of 13.4 mol% (based on $3^{EAA}/3^{total}$) or 12.6 mol% (based on $2^A/2^{total}$)

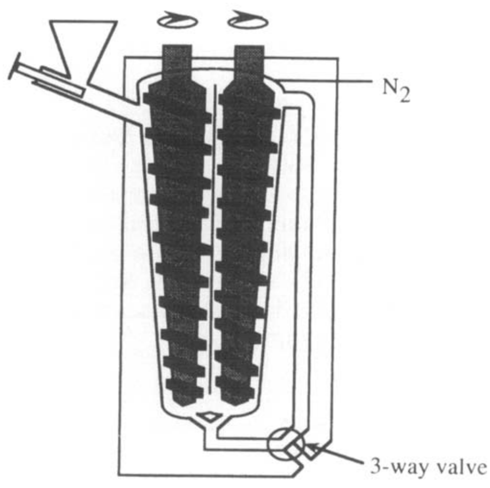


**Figure 2** DSM. (4 cc) mini-twin screw extruder

was ascribed to a methylene proton next to a urethane link. The terephthalic amide content ($X_A$-NMR $3^{EA}$) in PBTA equals $3^{EAA}/3^{total}$. When a peak from amide block sequences ($3^{AA}$) in PBTA is present, it overlaps with the $3^{EAA}$ peak and the determination of pure $3^{EAA}$ is not possible.

### *Aim*

The aim of this study is to investigate the change in the $T_g$ of the PC phase due to interchange reactions during melt blending of PC/PBT and PC/PBTA.

## EXPERIMENTAL

### *Materials*

PBT and PBTA20 (with 20 mol% diamide) were synthesized and their properties are given in *Table 2*[6]. PC (Lexan 125, MW 23 000 and Lexan 145, MW 26 000 g mol$^{-1}$), were kindly supplied by GE Plastics (Bergen op Zoom). TPPi was purchased from Aldrich (>97% purity) and used as received. The polymers were dried at 100°C in vacuum overnight before blending and testing.

### *Melt blending*

The PC-blends with PBT and PBTA20 were mixed with a 4 cc mini-twin screw extruder (DSM Research, Geleen, The Netherlands) (*Figure 2*). The set temperature for all the samples was 270°C and the screw speed was 30 rpm. PBT (PBTA20) and TPPi were dry mixed, and added together with PC to the extruder. With a closed valve, batches of about 4 g of material were mixed. With an open valve (no recirculation) any yield was possible and the residence time was approximately 2 min. The extrudate was cooled in water and cut in pieces.

### *Solution blending*

Solution casting was performed according to a procedure reported by Hanrahan[21]. PC and PBT (PBTA20) were dissolved in 1,1,1,3,3,3-hexafluoro-2-propanol (2 wt%) at room temperature (R.T.) and the solution was cast on a glass plate. The film was dried at R.T. overnight and subsequently at 150°C for 5 h in vacuum. Blending by solution precipitation was performed according to a procedure reported by Montaudo[22]. PC and PBT (PBTA20) were dissolved in hot phenol/1,1,2,2-tetrachloroethane (36/64 wt%) (about 13 g dl$^{-1}$). The polymers were co-precipitated in ethanol, washed twice with ethanol and dried at 60°C in vacuum overnight.

### *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 bars, respectively, was applied. The mould was cooled (about 10°C min$^{-1}$) and the specimen released.

### *Viscometry*

The inherent viscosity $\eta_{inh}$ was measured at a 0.5 g dl$^{-1}$ solution in phenol/1,1,2,2-tetrachloroethane (36/64 wt%) using a capillary Ubbelohde 1b at 25.0 ± 0.05°C.

### *Differential mechanical analysis*

D.m.a. was performed with a Myrenne ATM3 torsion pendulum. The loss moduli $G''$ were determined as a function of temperature, at 1 Hz, with the maximum of $G''$ taken as glass transition. The heating rate was 1 ±

**Table 2** Properties of PC, PBT and PBTA

| Polymer | $\overline{M_w}$ (g mol$^{-1}$) | $\eta_{inh}$ (dl g$^{-1}$) | $T_{m2}$[a] (°C) | $\Delta H_m$ (°C) | $T_{g2}$ (d.s.c.) | $T_{g1}$ (d.m.a.) |
|---|---|---|---|---|---|---|
| PC (Lexan 125) | 23 000 | 0.50 | – | – | 145 | 144 |
| PC (Lexan 145) | 26 000 | 0.54 | – | – | 147 | 145 |
| PBT-2 | | 1.39 | 212 + $\underline{220}$ | 42 | | 47 |
| PBTA10 | | 2.12 | 201 + $\underline{229}$ | 62 | | 60 |
| PBTA20-52A | | 1.08 | 224 + $\underline{252}$ | 20 | | 66 |
| PBTA25-2A | | 0.96 | $\underline{263}$ | 28 | | 75 |

[a] The main melting peak is underlined

$0.5°C\,min^{-1}$. The torsion bar (about $70 \times 9 \times 2\,mm^3$) was dried at 100°C in vacuum overnight before analysis.

*D.s.c.*

A Perkin-Elmer DSC7 equipped with a PE-7700 computer and TAS-7 software was used to analyse the melting and crystallization transitions at a heating and cooling rate of $20°C\,min^{-1}$. The peak maximum was taken as the transition temperature for $T_m$ or $T_c$ and the area under the curve as $\Delta H$. The $T_g$ was defined as the temperature halfway up the heat capacity jump. Tin was used as calibration standard.

*N.m.r.*

$^1H$ n.m.r. spectra were recorded on a Bruker AC 250 spectrometer at 250.1 MHz. Deuterated trifluoroacetic acid/chloroform (40/60 vol%) was used as solvent with TMS as internal standard.

*Elemental analysis*

The lithium (Li) content was measured by flame emission spectroscopy (AES) with a Varian AA6, or by atomic absorption spectroscopy (AAS) with a Perkin Elmer 500. Titanium (Ti) was detected by X-ray fluorescence in a XRF PW 1480. The nitrogen (N) content was measured with an Elemental Analyzer 1106 using gas chromatography. From the measured N-content the actual amide content ($X_A$) was calculated.

*Endgroup analysis*

The amino endgroup content was determined using a Titroprocessor Metrohm 636 equipped with a Dosimat E635. Solutions of PBTA in phenol/water (85/15 vol%) were titrated with trifluoromethane sulfonic acid (TFMS) in tertiary butanol (0.1 M).

## RESULTS AND DISCUSSION

### *PC/PBT and PC/PBTA without phosphites*

Blends of PC/PBT (70/30) and PC/PBTA20 (70/30) were prepared in solution and by melt mixing. The solution cast and solution precipitated systems represent physical mixtures of PC and PBT or PBTA20. In the melt blended system transesterification reactions may also have occurred. The change in the glass transition temperature of the PC-phase is a measure of the solubility of PBT or PBTA20 in PC.

The thermal properties of these blends were studied with d.s.c. The first heating scan at $20°C\,min^{-1}$ indicates the $T_{g1}$ directly after blending. Subsequently, the samples were kept in the melt at 260°C (PC/PBT) or 270°C (PC/PBTA) for 5 min, quenched with $200°C\,min^{-1}$ to 30°C and sample reheated at $20°C\,min^{-1}$ ($T_{g2}$, $T_{m2}$, $\Delta H_{m2}$). After the second heating cycle the degree of transesterification ($r$) was determined by $^1H$ n.m.r.

*Solution casting.* For solution casting, PC/PBT (70/30) (*Table 3*, no. 1) and PC/PBTA20 (70/30) (no. 4) were dissolved in 1,1,1,3,3,3-hexafluoro-2-propanol at room temperature. Without stirring the solution appeared to be separated in a PC-rich and a PBT (PBTA20)-rich liquid phase indicating a different degree of polymer–solvent interaction[23]. During evaporation of the solvent, an inhomogeneous film was formed. The high $T_{g1}$ of the PC-phase in PC/PBT (*Table 3*, no. 1) and in PC/PBTA20 (no. 4) indicate a high degree of phase separation in these blends and a solvent-induced phase separation may have occurred[22,24]. The high $T_{g1}$ of PC may also be partly ascribed to crystallization of PBT, as reported by Hobbs[24] and Birley[25].

After a thermal treatment for 5 min it appeared that the $T_{g2}$ of the PC-phase in PC/PBT and PC/PBTA20 remained relatively high. However, the melting temperature and heat of melting of PBT ($T_{m2}$ and $\Delta H_{m2}$) had decreased. The melting peak of PBTA20 disappeared after 5 min at 270°C in the d.s.c.-pan. This reduction in the melting heat of PBT and PBTA20 in the cast blends could not easily be explained. The amount of dissolved PC in PBT is expected to be minimal and the degree of transesterification was in both cases below the detection limit of $^1H$ n.m.r. (about 0.2 mol%).

*Solution precipitation.* Precipitation of PC/PBT (*Table 3*, no. 2) and PC/PBTA20 (*Table 3*, no. 5), both dissolved in phenol/1,1,2,2-tetrachloroethane, occurred with ethanol. The voluminous precipitate appeared white and contained less than 30 ppm Ti (44 ppm expected). Thus impurities and titanate residues in PBT and

**Table 3** PC/PBT and PC/PBTA20 (70/30 wt%), thermal properties after blending without phosphites

| Sample | Blend no. | Blending method | $T_g$ of PC | | $T_{m2}$ (°C) | $\Delta H_{m2}$ ($J\,g^{-1}$ PBTA) | Transesterification ($r$) (mol%) |
|---|---|---|---|---|---|---|---|
| | | | $T_{g1}$ | $T_{g2}$ | | | |
| PC Lexan 145 | – | – | 147 | 147 | – | – | – |
| PBT-2 | – | – | – | – | 219 | 37 | – |
| PC/PBT | 1 | casting | 152 | 146 | 180 | 17 | <0.2 |
| PC/PBT | 2 | precipitation | 147 | 106 | 215 | 57 | <0.2 |
| PC/PBT | 3 | prec. + melt | 102 | 96 | 213 | 63 | 0.4 |
| PC Lexan 145 | – | – | 147 | 147 | – | – | – |
| PBTA20-52A | – | – | – | – | 251 | 30 | – |
| PC/PBTA20 | 4 | casting | 151 | 145 | n.d. | | <0.2 |
| PC/PBTA20 | 5 | precipitation | 148 | 145 | 253 | 53 | <0.2 |
| PC/PBTA20 | 6 | prec. + melt | 145 | 141 | 250 | 27 | 0.5 |
| PC/PBTA20 | 7 | melt | 117 | 101 | n.d. | | 23 |
| PC Lexan 125 | – | – | 145 | 145 | – | – | – |
| PBTA20-7A | – | – | – | – | 247 | 34 | – |
| PBTA20-7Aprec. | – | – | – | – | 247 | 45 | – |
| PC/PBTA20 | 8 | melt | 144 | 138 | 251 | 15 | <0.2 |

n.d. = not detectable

PBTA20 were partly removed by this precipitation method. This indicates the presence of strong Ti-PBTA interaction or the co-precipitation of Ti-compounds. Chatterjee[26] reported other methods, fractionation and chelation with acetyl acetone, but even then a total removal of Ti residues was not achieved.

Directly after precipitation the $T_{g1}$ of PC/PBT was high (147°C) (*Table 3*, no. 2). The $T_{g2}$ was considerably lower (106°C). The $T_{m2}$ of PBT decreased to 215°C but its $\Delta H_{m2}$ remained high. The degree of transesterification remained below 0.2 mol%.

The $T_g$ of PC in solution precipitated PC/PBTA20 (*Table 3*, no. 5) decreased from 148°C ($T_{g1}$) to 145°C ($T_{g2}$). The melting peak of PBTA20 in the blend was not different from that of the neat polymer and the degree of transesterification was not detectable. Thus significant transesterification appears not to take place during the thermal treatment of precipitated PC/PBTA20 in the DSC.

*Melt blending solution precipitated blend.* Melt blending of the solution precipitated blends (*Table 3*, nos 3 and 6) was carried out in a mini twin screw extruder (2 min at 270°C) without phosphites being added. The PC/PBT blend (no. 3) immediately transesterified into a blend with a $T_{g1}$ of 102°C, which is comparable with the precipitated blend after 5 min at 260°C in the d.s.c. ($T_{g2}$, no. 2). After a further 5 min in the melt in the d.s.c. the $T_{g2}$ was 96°C. In the sample some transesterification had taken place. The precipitated PC/PBTA20 blend (no. 6), on the other hand, had a high $T_{g1}$ and a high $T_{g2}$. In this blend some transesterification had also taken place.

The low degree of transesterification after melt treatment of precipitated blends suggests that the titanate catalyst has largely been inactivated by the solution precipitation method. To confirm this hypothesis, two experiments were carried out. One where only the PBTA was solution precipitated (PBTA20-7A in *Table 3*) before melt blending (no. 8) and a direct melt blending without first a solution precipitation step (no. 7). Where only the PBTA was solution precipitated the degree of transesterification (no. 8) was still very low. A direct melt blending of PC/PBTA (no. 7) resulted in a low $T_{g1}$ (117°C), a low $T_{g2}$ (101°C) and a high degree of transesterification ($r = 23$ mol%). In this sample the melting peak had also disappeared.

The suppression of transesterification in melt blends of precipitated PC/PBTA20 may therefore be explained by an inactivation of titanate during solution precipitation. The titanate compound may have reacted with water, present in phenol (formation of inactive Ti-oxanes) or with phenol itself (formation of less active $Ti(OPh)_4$).

The shift in glass transition was also studied by d.m.a. The loss modulus ($G''$) of PC (Lexan 145), PBTA20 and sample no. 8 are given in *Figure 3*. The blend contains two $T_g$s and they were only slightly shifted towards each other. This suggests that blend no. 8 is a well separated phase blend.

The melting temperature of the PBTA20 is 30°C higher than PBT[5,6] and so the PC/PBTA20 blend has a 30°C higher melting temperature than PC/PBT. This higher melting temperature is a major advantage for high temperature dimensional stability.

The $T_{g1}$ of PC in PC/PBTA (70/30) blends as a function of amide content in the PBTA is presented in *Figure 4*. The solution cast and solution precipitated blends do not show transesterification, their $T_{g1}$ was high and hardly changed with amide content in PBTA. This minimal change of PC $T_g$ suggests a minimal mixing of the two phases. This minimal mixing might both be due to the minimal (not measurable) amount of transesterification and the possible large phase structures due to the precipitation method. The melt mixed precipitated blends which showed only minimal amount of transesterification, the $T_{g1}$ decreased due to this melt blending. The $T_g$ decrease was, however, less with increasing amide content. Melt mixing considerably improves the mixing of the components. The increase of $T_{g1}$ with amide content in PBTA suggests that with no or minimal transesterification the miscibility of PBTA in PC decreased as amide content increases.

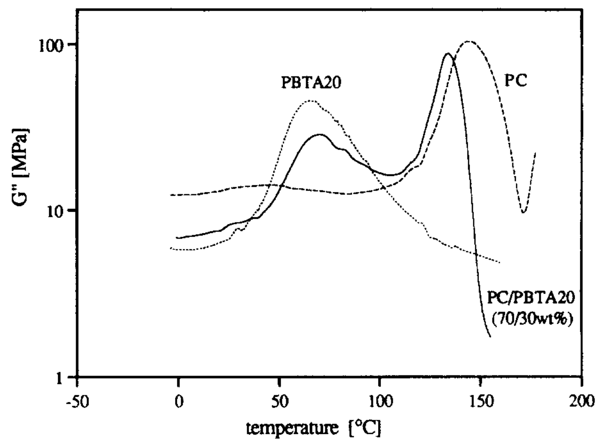


**Figure 3** $G''$ modulus as a function of temperature of: PC (Lexan 145) and PBTA20 and PC/PBTA20 blend (*Table 3*, no. 8)

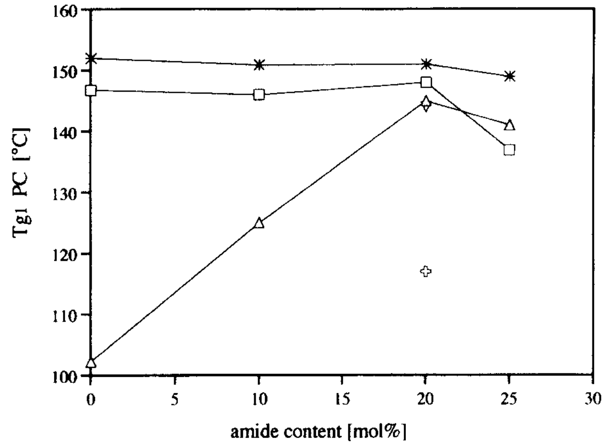


**Figure 4** The $T_g$ of the PC-phase as a function of the amide content in PBTA (d.s.c., first heating scan): *, casting; □, precipitation; △, precipitation and melt blending, ▽, prec. PBTA and melt blending, +, direct melt blending

Direct melt blending of PC and PBTA20 resulted in a strong decrease of the $T_g$ of the PC-phase, the sample was also highly transesterified. With this transesterification the miscibility is strongly increased.

PC $T_g$ is high if no mixing takes place. In a well mixed PC/PBT system the $T_g$ is, in the absence of transesterification, greatly lowered. With increasing amide content in PBTA miscibility decreases. If transesterification has taken place the miscibility strongly increases lowering the $T_g$. So with PBTA in absence of

**Table 4** Influence of triphenyl phosphite concentration on the blend properties of PC/PBTA20 (70/30 wt%)

| TPPi | | | | | |
|---|---|---|---|---|---|
| (wt%) | (2TPPi/Ti) | $\eta_{inh}$ (dl g$^{-1}$) | $r$ (mol%) | $T_{g1}$ (°C) | $X_A$ n.m.r. (mol%) |
| 0 | 0 | 0.79 | 4.0 | 117 | 14.7 |
| 0.37 | 8 | 0.76 | 0.3 | 137 | 17.9 |
| 0.74 | 16 | 0.76 | n.d. | 142 | 19.4 |
| 1.09 | 24 | 0.73 | n.d. | 135 | 18.8 |
| 2.18 | 48 | 0.81 | n.d. | 126 | 19.0 |

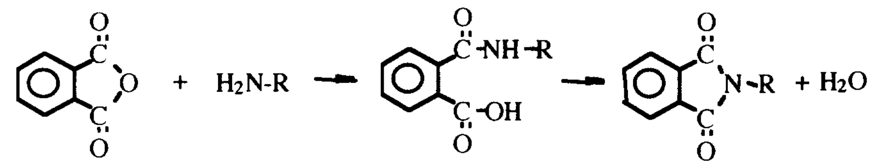
n.d. = not detectable

transesterification the PC $T_g$ of a well mixed blend remained high.

### *Effect of phosphites on PC/PBTA*

Due to transesterification the $T_g$ of the PC phase in the PC/PBT blend is lowered. The transesterification can be suppressed if the catalytic effect of titanate residues in PBT/PBTA can be inhibited. Triphenyl phosphite (TPPi) has been used to 'kill' the catalytic effect of titanate residues. For the formation of a stable, catalytically inactive, octahedral complex, at least 2 mol of TPPi is required per mol of titanate compound, $Ti(OR)_4$. Usually, an excess of TPPi is added to counter the loss of activity by incomplete homogenization, hydrolysis of TPPi or other side effects.

The influence of TPPi on the $T_g$ of the blends has been studied (*Table 4*, *Figure 5*). For comparison, the effect of TPPi on neat PC is also given. The $T_g$ of the neat PC decreases considerably with TPPi concentration. The TPPi is a plasticizer for PC. A melt mixed blend of PC/PBTA has considerable transesterification (*Table 4*) and with that a low $T_g$. Adding TPPi during the blending increases the $T_g$. However, at high TPPi concentrations the $T_g$ is lowered again. The initial increase in $T_g$ is due to the suppression of the transesterification (*Table 4*). The $T_g$ decrease at higher TPPi concentrations in the blend seems to be due to the plastication effect of TPPi on the PC. In our system an optimum was found at 0.5–1.0 wt% and this corresponds to 8–16 times molar concentration of TPPi over the titanate concentration. Deveaux[2] reported that an addition of 0.5 wt% TPPi for their PC/PBT was sufficient. At 8 times the titanate concentration the transesterification was nearly fully suppressed. That such a large excess is needed means too that the addition of TPPi during blending is not very efficient. Suppression of the transesterification without TPPi as in *Table 3*, no. 6 gives a higher $T_g$. Thus it can be expected that if the transesterification can be suppressed with less TPPi the $T_g$ of the blend will be higher as the excess TPPi acts as a plasticizer.


(5)

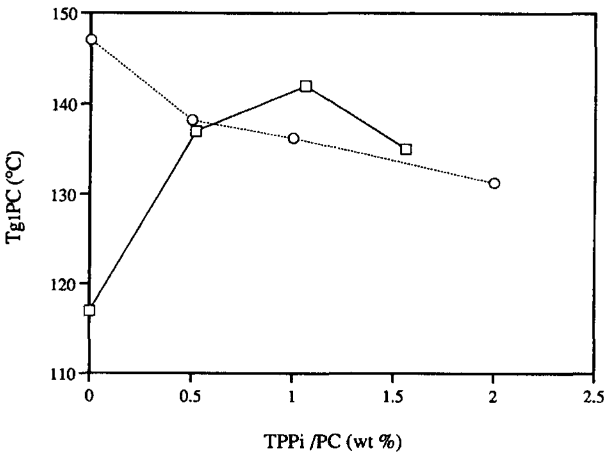


**Figure 5** $T_g$ of the PC-phase as a function of TPPi-content: ○, in PC; □, in PC/PBTA20 blend (70/30 wt%)

The terephthalic amide content ($X_A$ n.m.r. based on $3^{EA}$) in the PC/PBTA20 blends was less reduced due to the addition of TPPi, while the N-content was unchanged. This indicates that the TPPi also suppresses the ester-amide interchange, also probably by inactivation of the titanate catalyst.

### *Effect of $NH_2$-endgroups in PC/PBTA20*

Amino endgroups can degrade carbonate groups by aminolysis resulting in unstable urethane bonds and phenol endgroups (*Table 1*). Gallucci[27] reported that endcapping of amino endgroups in PC/PA blends is possible by a reaction with anhydrides which are added during melt blending. With this reaction stable terephthalic imide endgroups are formed and water is released (**5**). Phthalic acid anhydride (PAA) in one or, preferentially, two times the equivalent amino endgroup content, was preferred.

In *Table 5* the results of some experiments with PC/PBTA20 melt blends are given in which the PAA and TPPi concentration have been varied. A melt blend of PC/PBTA20 without PAA and TPPi (no. 9 in *Table 5*) shows a high degree of transesterification (8.1 mol%) and a low inherent viscosity. Both effects were ascribed to a combination of aminolysis of PC, thermal degradation and decomposition of transesterification products (butylene carbonate). After addition of an 8 times excess of TPPi (0.37 wt%) the transesterification has partly been suppressed; the amino endgroup content decreased by endcapping reactions of TPPi (no. 10).

As expected (no. 11) the addition of 2 mol of endcapper PAA per mol of $NH_2$-endgroup in PBTA20 reduced the amino endgroup content. Surprisingly, the degree of transesterification of PC/PBTA20 without TPPi also decreased after addition of PAA. We have not been able to explain the latter because inactivation of the Lewis acid $Ti(OR)_4$ by anhydrides is not very likely.

In PC/PBTA20 blends with PAA and TPPi (no. 12) almost all amino endgroups in PBTA20 were consumed. The degree of transesterification seemed to be somewhat lower than with either one of the stabilizers but the effect on the $T_g$ of PC in the blends was relatively small.

**Table 5** Effect of PAA and TPPi on PC/PBTA20 (70/30 wt%) blends, mixed 10 min at 270°C/35 rpm

| Sample | Blend no. | PAA/$NH_2$ (mol $mol^{-1}$) | 2TPPi/Ti (mol $mol^{-1}$) | $\eta_{inh}$ (dl $g^{-1}$) | $T_{gl}$ PC (°C) | $r$ (mol%) | $NH_2$ (meq $g^{-1}$ PEA) |
|---|---|---|---|---|---|---|---|
| PC Lexan 125 | – | – | – | 0.50 | 145 | – | – |
| PBTA20-7A | – | – | – | 0.80 | – | – | 0.033 |
| PC/PBTA20 | 9 | 0 | 0 | 0.45 | 106 | 8.1 | 0.030 |
| PC/PBTA20 | 10 | 0 | 8 | 0.57 | 129 | 2.6 | 0.013 |
| PC/PBTA20 | 11 | 2 | 0 | 0.49 | 112 | 3.9 | 0.007 |
| PC/PBTA20 | 12 | 2 | 8 | 0.47 | 131 | 1.3 | <0.003 |

**Table 6** Effect of Li-residues in PBT on PC/PBT blends (50/50 wt%) with 4 × 2TPPi/Ti, mixed 8 min at 260°C/30 rpm

| Sample | Blend no. | Li (ppm) | $\eta_{inh}$ (dl $g^{-1}$) | $T_g$ PBT (°C) DMA | $T_g$ PC (°C) DMA | $T_{gl}$ PC (°C) d.s.c. |
|---|---|---|---|---|---|---|
| PC Lexan 125 | – | 0 | 0.50 | – | 144 | 147 |
| PBT-4 | – | 0 | 0.53 | 47 | – | – |
| PBT-4A[a] | – | 0 | 1.60 | – | – | – |
| PBT-3 | – | 500 | 0.26 | – | – | – |
| PBT-3A[a] | – | 500 | 0.71 | – | – | – |
| PC/PBT | 13 | 0 | 0.91 | 61 | 117 | 128 |
| PC/PBT | 14 | 10 | 1.00 | 64 | 114 | 125–128 |
| PC/PBT | 15 | 50 | 0.98 | 72 | 128 | 130 |
| PC/PBT | 16 | 100 | 0.93 | 72 | 121 | 129 |

[a] A is after postcondensation in the solid state (24 h at 200°C in $N_2$)

### *Effect of Li-residues in PC blends*

Lithium catalyst may reside in PBTA to a relatively high extent. PBTA20 synthesized from purified T4T.dimethyl contained about 20–40 ppm Li[7]. It had initially been added as $LiOCH_3$ in the T4T.dimethyl synthesis and was partly removed by recrystallization of T4T. Lithium residues may be present in the polymer as lithium terephthalate or lithium hydroxide. These compounds are salts of relatively strong bases and therefore liable to induce degradation (by hydrolysis) of polycarbonate. Gallez[28] has studied lithium benzoate and especially sodium benzoate for their (heterogeneous) nucleating activity in the crystallization of PC. As a side-effect the salts appeared to catalyse the degradation of PC.

The effect of Li-residues on PC was tested on PC/PBT blends instead of PC/PBTA blends, in order to exclude any possible effect of Li on the stability of the amide in PBTA[20]. First a master batch of PBT with 500 ppm Li was synthesized, with the addition of $LiOCH_3$ (2 M in methanol) at 120°C before the transesterification stage. A blend range of different lithium residue concentrations was obtained (*Table 6*) by mixing the master batch with lithium-free PBT and PC (Lexan 125).

*Table 6* also shows the effect of Li-residues in blends of PC with PBT. An increasing concentration of lithium residue in PBT (blend nos 13–16) appeared to have little effect on the inherent viscosity of the blend. Probably lithium compounds were not active as strong bases with respect to the degradation of PC. In the case of lithium terephthalate endgroups, the Li–Te bond may have a more covalent character than the above mentioned Na-benzoate bond.

In spite of the low amount of TPPi, which may not have suppressed the transesterification completely, the effect of lithium residue on the miscibility of PC/PBT was only small. The glass transition of PBT increased slightly with increasing lithium content. The glass transition of PC, measured by means of d.m.a. and d.s.c., was not significantly affected.

### *Transesterification and miscibility*

The preceding experiments with PC/PBT and PC/PBTA20 blends have shown that transesterification (and carbonate–amide interchange) leads to an increase in miscibility. The formed block copolymers were probably located at the interface and caused a decrease of the interfacial tension of the two phases[29]. For PC/PBT it has been reported that with increasing degree of transesterification the morphology of the blend changes in steps. The starting polymers form a near immiscible two-phase structure with a coarse structure. Some transesterification leads to a finer dispersed structure. More transesterification leads to a partially mixed structure and eventually a one phase system is obtained[30].

The actual relationship between the miscibility, expressed by the glass transition of the PC-phase, and the degree of transesterification ($r$) has not yet been reported in the literature. The difficulty is that the $T_g$ depends both on the amount of transesterification and on the concentration of TPPi employed. In this section the properties of PC/PBT and PC/PBTA20 blended by different methods, of only the non-stabilized systems have been combined. *Figure 6* shows for PC/PBTA20 blends a strong decrease of the glass transition of the PC-phase with increasing degree of transesterification.

The results in *Figure 6* indicate that at an equivalent degree of transesterification, the extent of phase separation in PC/PBTA20 is higher than in PC/PBT.

The $T_g$ of the blends (at constant $r$) is further reduced if some TPPi is also present. The excess TPPi acts as a plasticizer for PC.

## CONCLUSIONS

The glass transition of the PC phase in PC/PBT and PC/PBTA blends depends on the miscibility of the polyester in the PC. The miscibility depends on the inherent miscibility and on the enhanced miscibility due to transesterification. The transesterification is catalysed

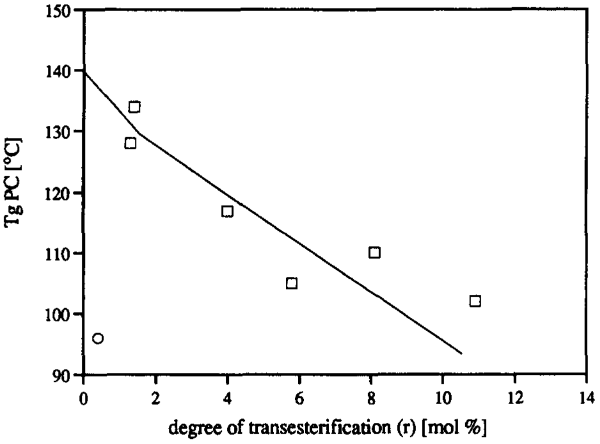


**Figure 6** $T_g$ of the PC-phase as a function of the degree of transesterification (no TPPi added); □, PC/PBTA20 (70/30) (wt%); ○, PC/PBT (70/30) (wt%)

by titanate catalyst residues in PBT(A). Direct melt blending of PC/PBT and PC/PBTA20 without reducing the activity of the titanate catalyst leads to a high degree of transesterification and complete miscibility.

Blends made by solution casting and precipitation were found to be fully phase separated systems with a high $T_g$ and a low titanate activity.

Melt mixed systems with a low degree of transesterification showed for PC/PBT a considerable lowering of the PC $T_g$ but for PC/PBTA20 this lowering was much less. The miscibility of PBT with PC is high but reduced if the PBT is modified with amide groups. With transesterification the $T_g$ is strongly lowered.

The transesterification can be suppressed by deactivating residual catalyst like phosphites. Triphenyl phosphite (TPPi) added during blending suppressed the transesterification and increased the $T_g$ of the system. However an 8–16 times molar excess relative to a complete complexation of $Ti(OR)_4$ had to be added for the highest $T_g$ and reduction of transesterification. An important side-effect of TPPi was a plastication of the PC-phase which lowered the maximal attainable $T_g$.

The lithium residue in PBTA was expected to have an effect on base-catalysed hydrolysis of PC. However, the presence of 100 ppm Li-residue in PBT did not affect the viscosity of the blend and the $T_g$ of the PC-phase.

The PC/PBTA blends have considerable higher melting temperatures than the PC/PBT blends which is important for the dimensional stability of the system.

## ACKNOWLEDGEMENTS

This research was financially supported by GE Plastics (Bergen op Zoom, the Netherlands). J. Feijen is acknowledged for the fruitful discussions and valuable suggestions.

## REFERENCES

1. Deveaux, J., Godard, P. and Mercier, J. P., *J. Polym. Sci., Polym. Phys. Ed.*, 1982, **20**, 1875.
2. Deveaux, J., Godard, P. and Mercier, J. P., *J. Polym. Eng. Sci.*, 1982, **22**, 229.
3. Kotliar, A. M., *J. Polym. Sci., Macromol. Rev.*, 1981, **16**, 367.
4. Porter, R. S. and Wang, L.-H., *Polymer*, 1992, **33**, 2019.
5. Gaymans, R. J., De Haan, J. L. and Van Nieuwenhuizen, O., *J. Polym. Sci.: Part A: Polym. Chem. Ed.*, 1993, **31**, 575.
6. Van Bennekom, A. C. M. and Gaymans, R. J., *Polymer*, 1996, **37**, 5439.
7. Van Bennekom, A. C. M. and Gaymans, R. J., *Polymer*, 1997, **38**, 657.
8. Valenza, A., La Mantia, F. P., Gattiglia, E. and Turturro, A., *Int. Pol. Proc.*, 1994, **IX**(3), 240.
9. Delimoy, D., Mélange de polycarbonate de bisphenol-A et de polybutylene terephthalat, Thesis, Academia Ed., Lovain-La-Neuve, 1988.
10. Aharoni, S. M., Hammond, W. B., Szobota, J. S. and Masilamani, D., *J. Polym. Sci., Polym. Chem. Ed.* 1984, **22**, 2579.
11. Aharoni, S. M., Forbes, C. E., Hammond, W. B., Hindenlang, D. M., Mares, F., O'Brien, K. and Sedgwick, R. D., *J. Polym. Sci., Polym. Chem. Ed.*, 1986, **24**, 1281.
12. Verhoeven, J. J. (GE Company, USA), EP 264143, 1990.
13. Golovoy, A., Cheung, M. F., Carduner, K. R. and Rokosz, M. J., *Polym. Eng. Sci.*, 1989, **29**, 1226.
14. Verhoeven, J. J. and Roovers, W. M. (GE Company USA), EP 295730 A1, 1988.
15. Zumstein van, F., *et al.* (Ceiba Geigy AG, Basel), DE 2751969 A1, 1978.
16. Kawase, S., Shima, T., Inata, H. and Kurisu, S., (Teijin Ltd, Japan), USP 3953539, 1976.
17. Bier, P. and Binsack, R., (Bayer AG, Germany), DE 2526827 C2, 1977.
18. Horn, W. E., (Borg-Warner Chemicals Inc., UK), USP 4385145, 1983.
19. Deveaux, J., Godard, P., Mercier, J. P., Touillaux, R. and Dereppe, J. M., *J. Polym. Sci.:,Polym. Phys. Ed.*, 1982, **20**, 1881.
20. Van Bennekom, A. C. M., Willemsen, P. A. A. T. and Gaymans, R. J., *Polymer*, 1996, **37**, 5477.
21. Hanrahan, B. D., Angeli, S. R. and Runt, J., *Polymer J.*, 1985, **17**, 297.
22. Montaudo, G., *J. Polym. Sci., Polym. Chem. Ed.*, 1993, **31**, 13.
23. Robard, A. and Patterson, D. G., *Macromolecules*, 1977, **10**, 706.
24. Hobbs, S. Y., Groshans, V. L., Dekker, M. E. J. and Schultz, A. R., *Polym. Bull.*, 1987, **17**, 335.
25. Birley, A. W. and Chen, X. Y., *Br. Polym. J.*, 1984, **16**, 77.
26. Chatterjee, A. M., Price, F. P. and Newman, S., *J. Polym. Sci.: Polym. Phys. Ed.*, 1975, **13**, 2369.
27. Gallucci, R. R. and Maresca, L. M. (GE Company, USA) USP 4749754, 1988.
28. Gallez, F., Legras, R. and Mercier, J. P., *Polym. Eng. Sci.* 1976, **16**, 276.
29. Wu, S., *Polymer Interface and Adhesion*. Marcel Dekker, USA, 1982, p. 122.
30. Tattum, S. B., Cole, D. and Wilkinson, A. N. Polymat 94, The Institute of Materials, London, Sept. 1994