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Polyesteramides based on PET and nylon 2,T
Part 3. Properties

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Abstract

The properties of polyesteramides based on PET and nylon 2,T (PETA) using DMT, the bis(esterdiamide) T2T-dimethyl (*N*,*N*′-bis(*p*-carbo-methoxybenzoyl)ethanediamine) and 1,2-ethanediol as starting materials has been studied. A PETA series with an increasing T2T content (0.1–30 mol%) has been synthesised and studied. It was observed by dynamic mechanical analysis, that the T_g, flow temperature (T_{fl}) and modulus of the rubbery plateau of PETA increased with increasing T2T content, implying a considerable improvement in the dimensional stability. The increase in T_g was approximately linear with T2T content. The T_m and T_{fl} were also increased with increasing diamide content. The increase in T_{fl} was non-linear, indicating that random co-crystallisation of the ester and amide segments did not occur. The amide segments are expected to self-assemble in the melt, and preferentially order with other amide segments. The crystallisation rate of PET was considerably improved by the incorporation of a small amount of T2T (0.1 mol%). By using higher concentrations of T2T, the crystallisation rate of PETA was improved even further. The crystallisation of PETA from the melt was studied using time-resolved WAXD measurements. It was observed that for $PETA_{25}$, crystalline amide segments were present at 310°C, this being well above the T_m measured by DSC (280°C). The hypothesis is that at high amide concentrations, small alternating segments are formed (amide–ester–amide), these have a much higher melting temperature and are present in their crystalline form above the melting temperature of the polymer. Upon cooling, these segments form the nucleation sites for PETA. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(ethylene terephthalate); Bis(esterdiamide1,2-Diaminoethane); Polyesteramides

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1. Introduction

Poly(ethylene terephthalate) (PET) is one of the most important polyesters. It has a high glass transition temperature (T_g) of 85°C and a high melting temperature (T_m) of 255°C. The major drawback in its application as an engineering plastic is its slow crystallisation rate, however, this can be improved by the addition of nucleators such as talc. An alternative way to improve the crystallisation rate is by the incorporation of diamide segments into the polyester chain [1,2].

In comparison to polyesters with a similar structure, polyamides have higher T_g and T_m values and crystallise rapidly, this being mainly the result of intermolecular hydrogen bonding of the amide groups. The disadvantage of polyamides is their high water absorption, in contrast, polyesters have a much lower water absorption. The favourable properties of polyesters and polyamides can, to a certain extent, be combined in polyesteramides polyesteramides, when the amide segments in the polyester are of a uniform length [1–3]. Amide segments of uniform length are present in alternating polyesteramides (PETA) and in polyesters modified with diamide segments. If the amide segments in the copolymer are randomly distributed, the copolymer is usually slow in crystallising and has a lower crystallinity [4,5]. For some applications a high heat resistance is required and the polymer should have a melting temperature in the region of 280°C. PET is therefore modified with T2T (one-and-a-half repeating unit of nylon 2,T) to obtain a polymer with a higher melting temperature.

1.1. Polyesteramides with diamide segments of uniform length

Williams et al. [3] have reported on the synthesis of PETA based on poly(hexamethylene terephthalate) (PHT) modified with 1,6-diaminohexane, using pre-formed bis(esterdiamides) (T6T-dimethyl (1)), in order to obtain a uniform length of the amide segment in the polyesteramide. In

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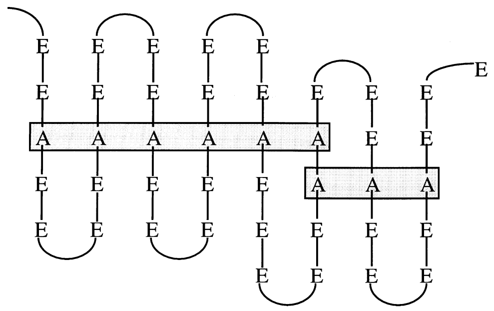
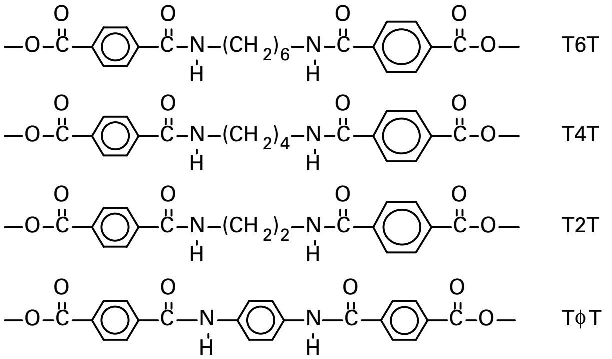


Fig. 1. Proposed scheme for an amide-adjacent crystallisation of $PBTA_{20}$, showing the ordering of (uniform) diamide segments and the disturbing effect of non-uniform amide segments [1].

going from the polyester to the alternating polyesteramide they were able to increase the melting temperature from 152 to 260°C.



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Van Bennekom et al. [1] have studied the properties of polyesteramides based on poly(butylene terephthalate) (PBT) and 1,4-diaminobutane (PBTA). By using the bis(esterdiamide) T4T-dimethyl as a monomer (**1**), it was possible to obtain a uniform amide segment length in the polyesteramide. Only one T_g was found by dynamic mechanical analysis, suggesting the presence of a homogeneous amorphous phase, the dependence of T_g on the amide content being almost linear. The T_m was found to gradually increase with increasing diamide content, although the crystalline structures of PBT and nylon 4,T are non-isomorphous. In varying the diamide content from 0 to 50 mol%, this led to an increase in the T_m from 225 to 320°C. A broadening of the melting peaks with increasing diamide content was observed in the DSC scans of the PBTA, thus suggesting a variation in lamellar sizes and composition.

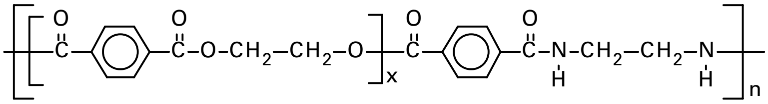
The ester and amide segments of PBTA are non-isomorphous and cannot co-crystallise from the melt, therefore, van Bennekom has proposed the following model for PBT modified with 20 mol% of diamide segments ($PBTA_{20}$). In the PBTA melt, the amide segments are able to self-assemble by the formation of hydrogen bonds; the ester segments follow by adjacent ordering. In this model the more rapidly crystallising amide segments form the nuclei for the crystallisation of the ester segments, this proposal is schematically represented in Fig. 1. In the presence of a non-uniform length of an amide segment, the plane of hydrogen bonding in a lamella will be disturbed (Fig. 1) and within that region, some dislocation of the hydrogen bonded network can be expected. With a decreasing uniformity of the amide segments, the melting temperature of $PBTA_{20}$ is decreased [6].

Van Bennekom has shown that the crystallisation rate of both PET and PBT can be increased by the incorporation of T4T segments. The incorporation of 2 mol% of T4T was found to be sufficient to decrease the undercooling ($T_m - T_c$) of PET from 77 to 63°C, whilst the crystallisation temperature (T_c) was increased from 180 to 193°C.

Yamada et al. [7] have modified PET with the bis(esterdiamide) TϕT (**1**). It was found that above a concentration of 6 wt%, the rigid segments of *p*-phenylene terephthalamide were aggregated as crystalline domains and that phase separation in the melt occurred. However, a fast nucleation without phase separation in the melt may be achieved by using a lower concentration of TϕT. Sakaguchi [8,9] has modified PET with arylate units and studied the effect on the crystallisation rate. Using random copolymers with rigid arylate units such as 4,4-biphenylene terephthalate or *p*-phenylene terephthalate at a concentration of 10 mol%, resulted in a crystallisation rate 2–3 times faster than that of PET.

The incorporation of T4T into PBT, or T6T into PHT, effectively replaces some of the ester bonds by amide bonds. The T2T segment (**1**) resembles the repeating unit of PET, in that it is of approximately the same length. Bussink et al. [2] have incorporated T2T into PET over a concentration range of 1.5 to 15 mol%. Incorporation of 1.5 mol% T2T into PET leads to a decrease in undercooling from 69 to 53°C as compared to pure PET. The co-polyesteramides based on PET and nylon 2,T are termed PETA (**2**). The synthesis and the thermal stability of PETA has been described previously [10].

The nucleating potential of several diamide segments (T4T, T2T and TϕT) in PET is studied, in addition, the properties of PETA with an increasing T2T content are also evaluated with the thermal and dynamic mechanical properties, the water absorption and the crystallisation rate of PETA from the melt being studied as a function of the diamide content.



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2. Experimental

2.1. Materials

1,4-Diaminobutane, *p*-phenylenediamine, dimethyl terephthalate (DMT), terephthaloylchloride, decanol, *N*-methyl-2-pyrrolidone (NMP), 1,2-ethanediol, tetraisopropyl orthotitanate ($Ti(i\text{-}OC_3H_7)_4$) (Ti), $Zn(CH_3CO_2)_2 \cdot 2H_2O$ (Zn) and Sb_2O_3 (Sb) were purchased from Merck, and used as received. $Ti(i\text{-}OC_3H_7)_4$ was diluted in *m*-xylene (0.1 M), T2T-dimethyl was synthesised and purified as described previously [11].

2.2. T4T-dimethyl

T4T-dimethyl was synthesised and purified according to route II for T2T-dimethyl [11] except that 1,2-diaminoethane was replaced by 1,4-diaminobutane. Following synthesis and washing, the product was recrystallised from NMP (50 g/l, 160°C).

2.3. TϕT-didecanyl

Terephthaloylchloride (100 g, 0.5 mol) was dissolved at room temperature in 400 ml NMP in a two-litre flask equipped with a mechanical stirrer, condenser, calcium chloride tube and nitrogen inlet. *p*-Phenylenediamine (16 g, 0.2 mol), previously dissolved in 400 ml NMP, was added slowly dropwise to the reaction mixture over a period of 3 h, following this, decanol (250 ml) was added dropwise and the temperature raised to 75°C. After 4 h, the reaction mixture was stopped and poured into a soxhlet extraction thimble, the product was washed twice with hot toluene and dried in a vacuum oven at 70°C overnight. The TϕT-didecanyl obtained was further purified by recrystallisation from NMP (125°C, 30 g/l) and washed twice with hot acetone and again dried in a vacuum oven at 70°C overnight.

2.4. Melt polymerisation of PET with low diamide content (<10 mol%)

The preparation of PET with 2 mol% T2T-dimethyl ($PETA_2$) is shown as an example, the reaction being carried out in a 250 ml stainless steel vessel with nitrogen inlet and mechanical stirrer. The vessel containing DMT (27.96 g, 0.144 mol), T2T-dimethyl (1.15 g, 0.003 mol) and 1,2-ethanediol (20.05 g, 0.323 mol) was heated in an oil-bath to 180°C and the catalyst solution (3 ml) added. After 40 min at 180°C the temperature was raised to 280°C (15°C/10 min) over a period of 60 min and after 10 min at 280°C the pressure was reduced to 20 mbar for 5 min and then further to less than 1 mbar for 15 min. The vessel was then cooled slowly to room temperature, whilst maintaining the low pressure.

2.5. Melt polymerisation of PETA (≥10 mol%)

The preparation of $PETA_{25}$ using a Zn/Sb catalyst system is shown as an example. Polymerisation using $Ti(i\text{-}OC_3H_7)_4$ as catalyst has been described previously [10]. The reaction was carried out in a 250 ml stainless steel vessel with nitrogen inlet and mechanical stirrer. The vessel containing DMT (19.42 g, 0.1 mol), T2T-dimethyl (19.22 g, 0.05 mol), 1,2-ethanediol (37–40 g, 0.6–0.65 mol) and zinc acetate (0.017 g, 0.076 mmol) was heated in an oil bath to 180°C. After 40 min at 180°C the temperature was raised to 290°C (15°C/10 min) over a period of 70 min. Antimony trioxide (0.022 g, 0.076 mmol) was then added and after 10 min the pressure was reduced to 20 mbar) for 5 min and then further to less than 1 mbar for 10 min. The vessel was then cooled slowly to room temperature, whilst maintaining the low pressure.

2.6. Solid state postcondensation

The polymer was ground in a Fritsch pulverisette (particle size <1 mm) and subsequently dried in a vacuum oven at 70°C overnight. Over a period of 24 h, the polymer was postcondensed in the solid state at a reduced pressure (0.1 mbar) in a glass tube which was placed in an oven at 220–230°C.

2.7. Viscometry

The inherent viscosity of the polymers at a concentration of 0.1 g/dl in *p*-chlorophenol at 45°C, was determined using a capillary Ubbelohde 1B.

2.8. Differential scanning calorimetry

Differential scanning calorimetry (DSC) spectra were recorded on a Perkin–Elmer DSC7 apparatus, equipped with a PE7700 computer and TAS-7 software. Dried sample (2–5 mg) was measured at a cooling and heating rate of 20°C/min. Firstly, the samples were heated to 320°C and after 2 min cooled to 20°C, the maximum in the cooling scan being taken as the crystallisation temperature. After a further 2 min, the sample was heated for the second time to 290°C. The maximum of the second heating scan being taken as the melting temperature, the peak area was used to calculate the enthalpy. For high melting polymers (>10 mol% T2T), the sample was rapidly heated to 340°C (80°C/min), and subsequent procedures were as described above.

2.9. Dynamic mechanical analysis

Samples for the Dynamic mechanical analysis (DMA) test ($70 \times 9 \times 2\ mm^3$) were prepared on an Arburg H manual injection moulding machine. The polymers were pre-melted in a mini-extruder and quenched in a water bath and dried prior to injection moulding. The barrel temperature of the injection moulding machine was set at about 50°C above the melting temperature of the polymer and the mould temperature was maintained at 150°C. The mould was opened after 2 min.

Table 1
DSC results of PET with different diamide segments prepared by copolymerisation, using $Ti(i\text{-}OC_3H_7)_4$ as a catalyst. Results of postcondensed polymers (at 225°C)

Diamide segment	Amide (mol%)	η_{inh} (dl/g)	T_m (°C)	ΔH_m (J/g)	T_c (°C)	ΔH_c (J/g)	ΔT (°C)
None	0	0.99	254	53	180	−38	74
T4T	2	0.32[a]	259	44	189	−43	70
TϕT	2	0.99	263	46	199	−49	64
T2T	2	0.94	264	51	206	−52	58

[a] Before solid state postcondensation.

Using a Myrenne ATM3 torsion pendulum at a frequency of approximately 1 Hz, the storage modulus G' and the loss modulus G'' were measured as a function of the temperature. Dried samples were first cooled to −100°C and subsequently heated at a rate of 1°C/min, the maximum of the loss modulus being taken as the T_g. The flow temperature (T_{fl}) was defined as the temperature where the storage modulus reached 15 MPa.

2.10. Water absorption

The absorption of water was measured as the weight gain after conditioning (see Eq. (1)). DMA test bars were dried at 100°C in a vacuum oven overnight and weighed (w_0). The samples were then conditioned in a dessicator over water at room temperature for 30 days and reweighed (w).

$$\text{absorption of water} = \frac{(w - w_0)}{w_0} 100\% \qquad [\text{wt\%}] \tag{1}$$

2.11. NMR

Proton NMR spectra were recorded on a Bruker AC 250 spectrometer at 250.1 MHz. Deuterated trifluoroacetic acid (TFA-*d*) was used as a solvent without an internal standard.

3. Results and discussion

3.1. Introduction

The diamide segments T4T and TϕT were incorporated into the polyester chain at a low concentration to study their effect on the thermal properties and the crystallisation behaviour of PET. The diamide segment T2T was incorporated into PET over a concentration range of 0.1 to 30 mol%. The thermal and dynamic mechanical properties and the water absorption of the PETA as a function of the amide content were studied, in addition to the crystallisation of PETA from the melt. A mechanism of crystallisation is also proposed.

3.2. Crystallisation of PET with different diamide segments

The nucleation of PET can be improved by the incorporation of diamide segments and a number of different diamide segments (T2T, T4T and TϕT, see (**1**)) have been studied for their ability to nucleate PET. These diamide segments were incorporated into PET by copolymerisation at a concentration of 2 mol%, using $Ti(i\text{-}OC_3H_7)_4$ as a catalyst. Table 1 shows the DSC-results for the postcondensed copolymers. The amide content in the polymer was determined by ^1H NMR.

The inherent viscosities of all the polymers were in the range of 1 dl/g and thus the molecular weights were high and comparable. It was found that the melting (T_m) and

Table 2
DSC-and DMA results of PET, using $Ti(i\text{-}OC_3H_7)_4$ as catalyst

T2T (mol%)	η_{inh} (dl/g)	T_m (°C)	T_c (°C)	η_{inh} (dl/g)[a]	T_m (°C)[a]	ΔH_m (J/g)[a]	T_c (°C)[a]	ΔH_c (J/g)[a]	T_g (°C)	T_{fl} (°C)	G' (150°C) (Mpa)
0		256	206	0.99	254	53	180	−38	88	244	72
0.1	0.38	260	212	1.03	264	45	210	−51			
0.25	0.69	260	212	n.s.[b]	261	47	206	−54			
0.5	0.60	260	208	n.s.[b]	260	51	205	−54			
1	0.35	261	208	1.08	262	44	206	−49			
2	0.77	261	210	0.94	264	51	206	−52			
4	0.49	264	217	0.94	264	39	212	−44			
10	0.43	258	214	0.50	265	47	216	−48	99	251	130
20		269	225	0.50	276	32	226	−28	106	259	140
25	0.11	269	226	0.55	269	8	234	−28	102	274	174
30	0.21	271		0.59	275	12	233	−6	112	287	188

[a] After solid state postcondensation.

[b] n.s.: not soluble in paa-chlorophenol.

Table 3
DSC and DMA results of PETA, using Zn/Sb as catalyst

T2T (mol%)	η_{inh} (dl/g)	T_m (°C)	T_c (°C)	η_{inh} (dl/g)[a]	T_m (°C)[a]	ΔH_m (J/g)[a]	T_c (°C)[a]	ΔH_c (J/g)[a]	T_g (°C)	T_{fl} (°C)	G' (150°C) (Mpa)
0	0.10	263	204	1.84	264	46	207	−48	88	247	67
10	0.14	252	208	0.67	268	47	219	−47	98	258	107
20	0.27	273	222	0.60	275	41	239	−36	108	273	136
25	0.15	268	220	0.64	282	37	247	−31	109	280	195
30	0.17	279		0.71	285	24	244	−17	118	>300	224

[a] After solid state postcondensation.

crystallisation temperature (T_c) of PET were both increased by the incorporation of diamide segments. As the crystallisation peak is sharper than that of the melting peak in the DSC spectrum, the ΔH_c value is taken as being more accurate than the ΔH_m value. These data show that the incorporation of diamide segments leads to an increase in ΔH_c to approximately 40–50 J/g, and therefore an increase in crystallinity.

All of the diamide segments were able to nucleate PET, as the undercooling was decreased. T2T was found to be the most effective nucleator, the undercooling being decreased from 74 to 58°C, a decrease of 16°C, indicating a considerable improvement in the crystallisation rate. This T2T segment is of approximately the same length as the repeating unit of PET, whereas the diamide segments T4T and TϕT are both somewhat longer than the repeating unit of PET. Although the T2T and ester segments of PET are expected to be non-isomorphous, T2T probably has a good fit in the crystalline lattice of PET.

3.3. Properties of PETA

A series of PETA based on PET and nylon 2,T (PETA) were synthesised with an increasing T2T content, the preformed bis(esterdiamide) T2T-dimethyl being used in order to obtain a uniform diamide segment length in the polymer. A series of PETA polymers with an increasing diamide content were synthesised using a titanium catalyst and DSC and DMA measurements were performed to study the thermal and the dynamic mechanical properties. The results are presented in Table 2.

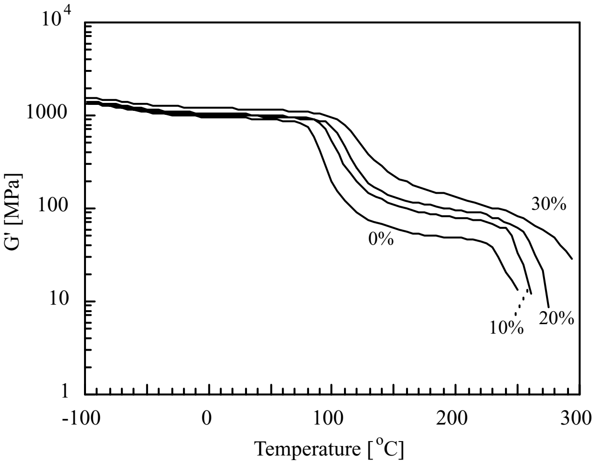

Fig. 2. Storage modulus (G') of PETA versus the temperature (T2T content in mol%).

The incorporation of a small amount of T2T (0.1 mol%) into PET results in a very large increase in the T_c (from 180 to 210°C) and also a small increase in the T_m. In using higher concentrations (≥10 mol%), the T_m and T_c can be further increased and the undercooling ($T_m - T_c$) further decreased. The enthalpies of melting (ΔH_m) and crystallisation (ΔH_c) both decrease with increasing T2T content. However, the melt and crystallisation peaks become broader and lower and therefore the T_m, T_c, ΔH_m and ΔH_c values obtained are less accurate. The dynamic mechanical properties were studied by DMA. It was found that the T_g, T_{fl} and modulus of the rubbery plateau all increase with increasing T2T content, therefore it can be concluded that the thermal properties of PET are profoundly improved by increasing the diamide concentration.

In contrast, the inherent viscosity is decreased at a T2T concentration greater than 10 mol%, the diamide concentration itself does not appear to have an influence. The presence of a small amount of amino endgroups in the bis(esterdiamide) already results in a lowering of the molecular weight. During polymerisation and solid state postcondensation degradation occurs. However the degradation rate of PETA using a zinc acetate/antimony trioxide (Zn/Sb) catalyst system was lower than when using titanium as a catalyst. Consequently, a series of PETA polymers was also synthesised using a Zn/Sb catalyst system. Table 3 shows the DSC and DMA results from this PETA series.

The inherent viscosities of PETA using the Zn/Sb catalyst system were found to be higher, with the properties of PETA such as T_g, T_m and T_{fl} being somewhat better than when using a titanium catalyst, probably as a result of the higher molecular weight obtained.

The influence of the diamide content in PETA on the glass transition, melting and T_{fl}, as well as water absorption and crystallisation from the melt are presented and discussed in a separate section. The polymers synthesised using the Zn/Sb system are being used in this evaluation.

3.4. Dynamic mechanical analysis

DMA tests were performed using a torsion pendulum

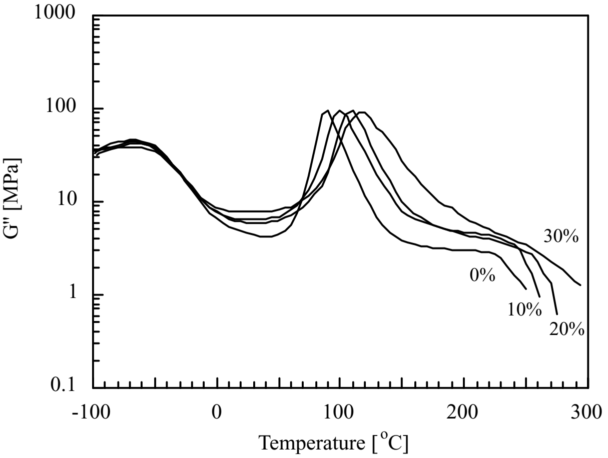

Fig. 3. Loss modulus (G'') of PETA versus the temperature (T2T content in mol%).

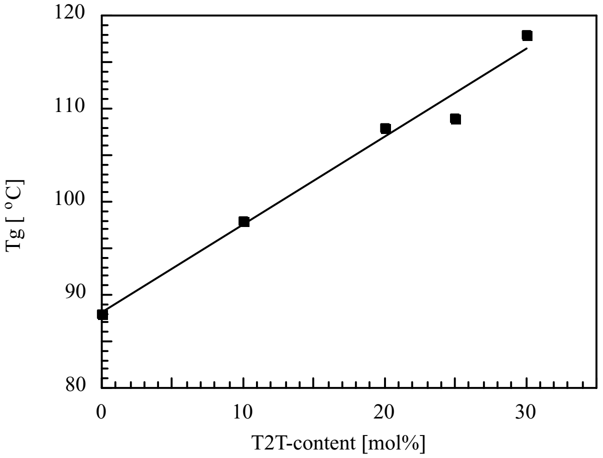

Fig. 5. T_g versus the T2T content of PETA.

apparatus, the storage modulus (resistance against the applied torque) and the loss modulus (dissipated energy) being determined with increasing temperature. The T_{fl} is defined as the temperature where the storage modulus (G') reaches 15 MPa, the maximum of the loss modulus (G'') is defined as the T_g. Fig. 2 shows the storage modulus of PETA plotted against the temperature.

Both of the values for T_g and T_{fl} increase with increasing T2T content. The storage modulus at 150°C, i.e. G' (150°C) (Table 3), is a measure of the modulus of the rubbery plateau, which increases with increasing crystallinity. The height of the rubbery plateau increases with increasing diamide concentration, resulting in a considerable improvement in the dimensional stability of the PETAs. Fig. 3 plots the loss modulus of PETA versus the temperature.

In this figure it can be seen that there is a sharp peak at the T_g, with this peak shifting towards the higher temperatures with an increasing amide content. Only one T_g is observed for PETA, indicating that there is one amorphous phase. At the T_{fl}, the values for both the storage (G') and the loss modulus (G'') fall.

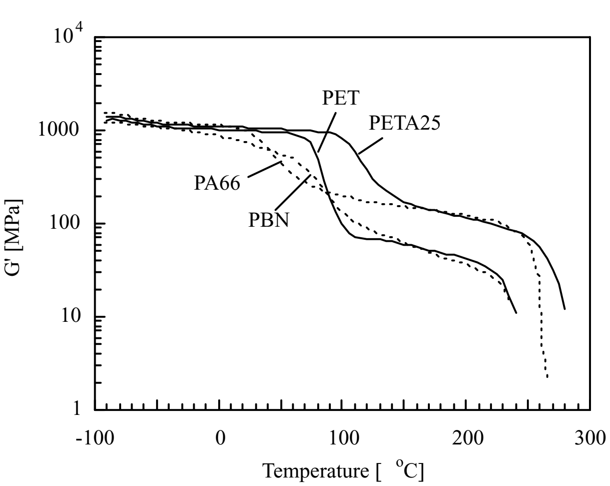

Fig. 4. Storage modulus of PET, PETA$_{25}$, PA6,6 and PBN versus the temperature.

Fig. 4 shows the storage modulus of PET, PETA$_{25}$, poly(butylene naphthalate) (PBN) and polyamide 6,6 (PA6,6) plotted against the temperature. PETA$_{25}$ is a rapidly crystallising polymer, with an undercooling ($\Delta T = T_m - T_c$) of 35°C, this being comparable to PBT. In comparison with other engineering plastics, PETA$_{25}$ has a high T_g (109°C), T_{fl} (280°C) and a high modulus in the rubbery plateau, and therefore a high dimensional stability.

3.5. Glass transition temperature

The T_g indicates the temperature at which the chain segments undergo co-ordinated molecular motions [12], it is determined from DMA measurements and is defined as the maximum of the loss modulus (G''). Fig. 5 shows the T_g of PETA plotted against the diamide content. PETA contains two-types of monomers, these being esters and amides, but appears to have only a single T_g, suggesting a homogeneous amorphous phase.

The T_g was found to increase with increasing diamide content. This is because the amide groups are able to form

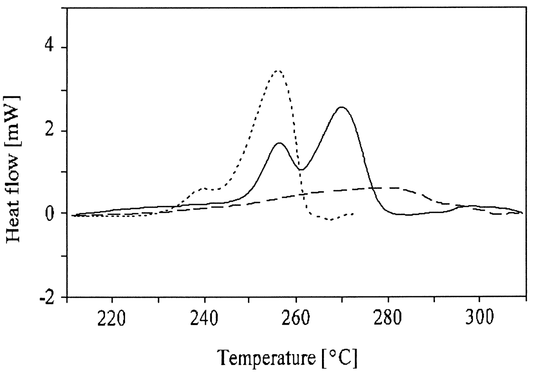

Fig. 6. Broadening of the melting peak of PETA with increasing amide content.

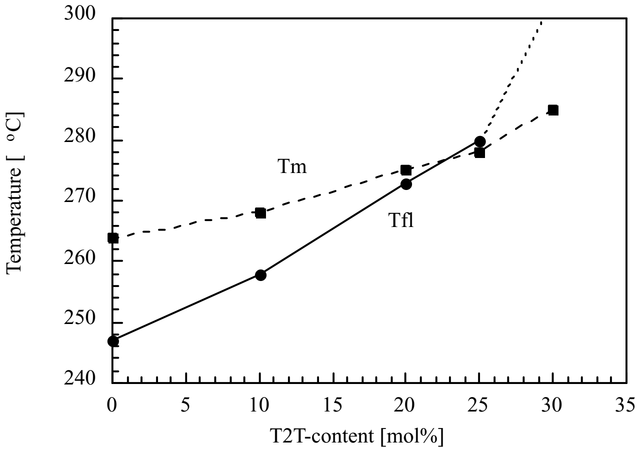

Fig. 7. T_m and T_{fl} versus the T2T content of PETA.

hydrogen bonds, resulting in increased intermolecular interactions and a decreased mobility of the polymer chain. The incorporation of diamide segments also leads to a more rapid rate of crystallisation and a higher crystallinity. The T_g of PET is sensitive to the crystallinity of the polymer [13]. As the PET crystallites are small, an increase in crystallinity affects the number of physical cross-links and therefore the mobility of the polymer chains. In changing from PET to PETA$_{30}$, the T_g increases in a linear fashion from 88 to 118°C, a similar effect being found in the PBTA system [1] (PBT modified with the diamide segments T4T).

3.6. Melting temperature

The T_m is defined as the ratio between the heat of melting (ΔH_m) and the entropy of melting (ΔS_m). ΔH_m is dependent on cohesion and intermolecular forces whereas ΔS_m depends on parameters such as the regularity of arrangements and the flexibility of the polymer chains. In general, the high melting temperature of PETA is due to a low ΔS_m value because of the associations still existing in the melt. Both the T_m and ΔH_m are measured by DSC.

Fig. 6 shows the DSC melting peaks of PETA as a function of increasing amide content. It can be seen that there is a shoulder in the melting peak of PETA, this feature is not unusual for polyesters and polyamides and can be attributed to a crystal rearrangement to a more stable, lamellar organisation. The DSC peaks become broader and lower with an increasing amide content and are therefore less accurate. This broadness suggests the presence of a wide variety of lamellar sizes and compositions, some lamellar sections having a higher amide content than others.

The T_{fl} was determined by dynamic mechanical analysis (DMA), this indicates the onset of the melting temperature. Fig. 7 plots both the T_m (DSC) and T_{fl} (DMA) versus the diamide content of PETA.

The T_m of a copolymer is usually depressed on lowering the chain order. However, by using amide segments of uniform length, both the T_m and T_{fl} of PETA are shown to increase with increasing diamide content. The increase of T_{fl} is steeper than that of T_m and even intersects the T_m line. At higher amide concentrations ($\geq$20 mol%), T_{fl} can be measured more accurately than T_m, due to a broadening in the melting peaks in the DSC spectrum.

The increase in T_{fl} is non-linear, indicating that random co-crystallisation of the ester and amide segments did not occur. According to the model proposed by van Bennekom (see Fig. 1), a nano-ordering of the amide segments in the melt would be expected to take place, with the amide segments preferentially ordering with other amide segments.

Table 4
Results of water absorption of PET and PETA$_{25}$ during 30 days at RT, 100% RH

Polymer	Water absorption (wt%)
PET	0.61
PETA$_{25}$	0.64

3.7. Water absorption

Polyamides are known to have a high degree of water absorption (up to 15 wt%) which causes a decrease in the T_g on wetting, in contrast, polyesters have a much lower water uptake. For example, PBT has a water absorption of 0.5 wt%. Gaymans et al. [14] have measured the water absorption of PBTA, PBT modified with the diamide segment T4T, at 25°C at 100% RH over a period of 30 days. At a low amide content there is an almost linear increase in the water absorption. PBTA$_{15}$ has a water absorption of 0.7 wt%, the amide groups being the main sites for hydrogen bonding of the water molecules. The water absorption of PET and PETA$_{25}$ was measured over a period of 30 days at room temperature and at 100% RH, the results being presented in Table 4.

The water absorption of PETA$_{25}$ is slightly higher than that of PET. The crystalline phase is not very accessible to water molecules and the water absorption predominantly takes place in the amorphous phase. This suggests that the diamide segments are present mainly in the crystalline phase, however, the observed increase in the T_g with increasing diamide content indicated that the diamide segments are also present in the amorphous phase. The amide segments may not be able to provide a site for water absorption because the polyester matrix prevents swelling of the polymer chains.

3.8. Crystallisation from the melt

The undercooling ($T_m - T_c$) is a measure of the crystallisation rate of polymers, with a small undercooling indicating a fast crystallisation. It has been shown that the undercooling of PET is decreased by the incorporation of small amounts (0.1 mol%) of T2T (see Table 2), incorporation

Table 5
DSC results of PETA with increasing T2T content, used for time-resolved WAXD measurements (synthesised with a Zn/Sb catalyst system)

T2T-content(mol%)	η_{inh} (dl/g)	T_m (°C)	ΔH_m (J/g)	T_c (°C)	ΔH_c (J/g)	ΔT (°C)
0	0.80	264	51	207	−52	56
0.1	0.76	264	51	209	−54	55
1	0.64	268	45	217	−46	51
10[a]	0.89	266	53	217	−46	49
25[a]	0.73	277	45	243	−22	34

[a] Postcondensed in the solid state at 230°C.

of higher percentages (≥10 mol%) results in an additional decrease in the undercooling. A series of PETA polymers was synthesised with increasing amounts of T2T using the Zn/Sb catalyst system, the results being shown in Table 5. The crystallisation from the melt was studied using time-resolved, wide angle X-ray diffraction (WAXD). To be able to compare the crystallisation behaviours, the molecular weights of the polymers should be approximately the same. The polymers with a low amide content (up to 1 mol%) were polycondensed in the melt for half an hour, those containing 10 and 25 mol% T2T were polycondensed in the melt for 10 min and subsequently postcondensed in the solid state at 230°C. The inherent viscosity of the polymers was in the range 0.8 g/dl, this being the norm for commercial PET. The same trends were observed for this series of polymers, as in the PETA series presented in Table 3. Fig. 8 shows the T_m and T_c versus the diamide content.

The undercooling was improved by the incorporation of a small amount of T2T, however the effect was less strong than in the titanium catalysed series (see Table 2), as the catalytic remnants (Zn/Sb) also nucleate PET(A). Titanium catalysts are known to be poor nucleators of PET, whereas antimony based catalysts are known to increase the rate of nucleation [15]. The crystallisation rate is further increased by using higher concentrations of T2T(>10 mol%).

It has been suggested that on cooling, the diamide segments in PETA pre-order in the melt [1]. Diamide segments in an amorphous polyester phase are only able to form thin lamella, having a low-melting temperature [16]. However, it is expected that an ester segment containing a diamide segment orders more easily than one containing just ester groups. This improved ordering results in a more rapid crystallisation. An additional possibility is that by having the diamide segments randomly distributed in the polyester chain, there will be a certain number of diamide segments that are present with just one diol between them, thus forming alternating amide–ester–amide segments (AAEEAA). Assuming that the diamide segments are randomly distributed in the polymer chain, for PETA$_{10}$ it is expected that there is 1 mol% of amide–ester–amide segments present. PETA$_{25}$ is expected to contain 6 mol% of amide–ester–amide segments. Alternating amide–ester–amide segments in an amorphous matrix have a high melting temperature [16], this being even higher than the melting temperature of PET, and are therefore expected to crystallise before the PETA. The crystallised amide–ester–amide segments may then act as nucleation sites for PETA.

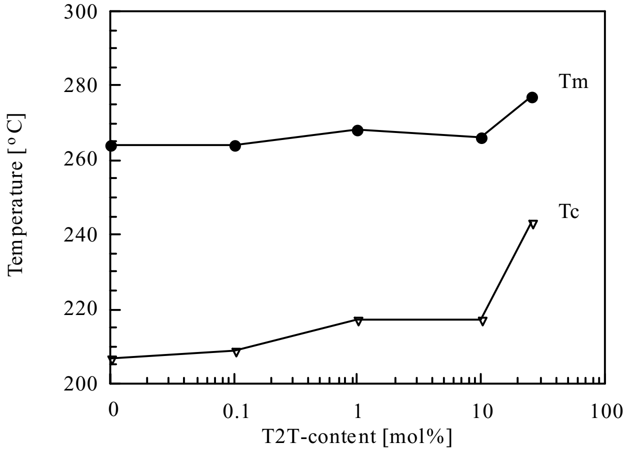

Fig. 8. T_m and T_c of PETA versus the T2T content (using Zn/Sb as catalyst system).

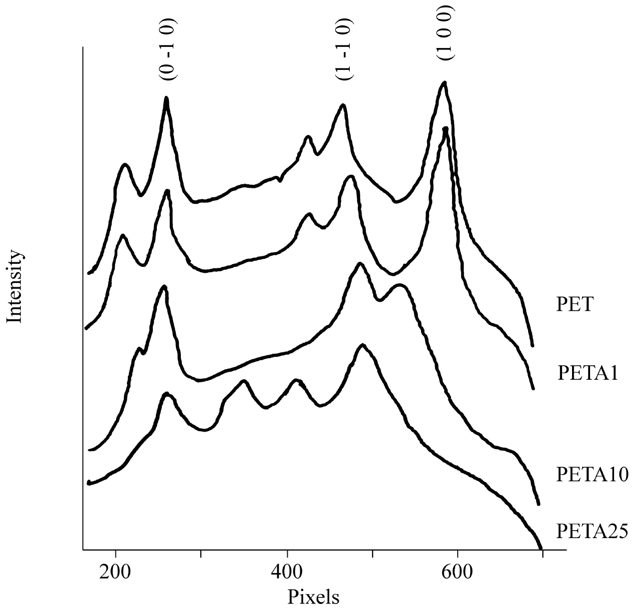

Fig. 9. WAXD pattern of PET, PETA$_{10}$ and PETA$_{25}$ at 150°C, after crystallisation.

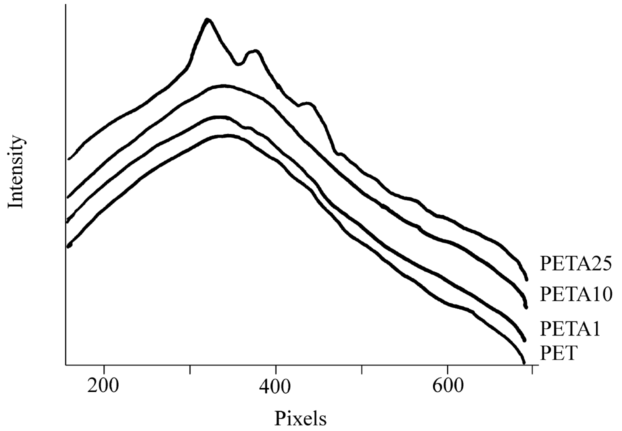

Fig. 10. WAXD pattern of PET, PETA$_1$, PETA$_{10}$ and PETA$_{25}$ in the melt.

To study the effect of the diamide concentration on the crystallisation rate of PET, time-resolved WAXD measurements were performed on polymers cooling from the melt at a rate of 10°C/min, starting at 300°C (PETA$_{25}$ from 315°C). Fig. 9 shows the WAXD patterns of the crystallised PETAs after cooling to 150°C. Three major peaks were indexed using the cell parameters for PET described according to Hall [17], the cell parameters being $a = 4.48$ Å, $b = 5.89$ Å, $c = 10.71$ Å, $\alpha = 99.8°$, $\beta = 117.6°$ and $\gamma = 111.5°$. PETA$_{0.1}$ and PETA$_1$ exhibit the same WAXD pattern as PET whereas PETA$_{25}$ has a completely different pattern, PETA$_{10}$ lies in-between PET and PETA$_{25}$. It is clear that the diamide units have a different cell structure as compared to PET and that PET and nylon 2,T are not isomorphous.

The diffraction patterns of the melts were also recorded (see Fig. 10), the melts of PET, PETA$_1$ and PETA$_{10}$ being amorphous. However, the WAXD pattern of the melt of PETA$_{25}$ at a temperature of 310°C exhibited sharp reflections (crystalline phase) at the top of a broad peak (amorphous phase). At 310°C (which is well above the peak maximum of the melting temperature according to DSC), PETA$_{25}$ clearly has some crystalline material remaining. In the diffraction pattern of PETA$_{25}$ at 310°C the crystalline ester peaks are absent.

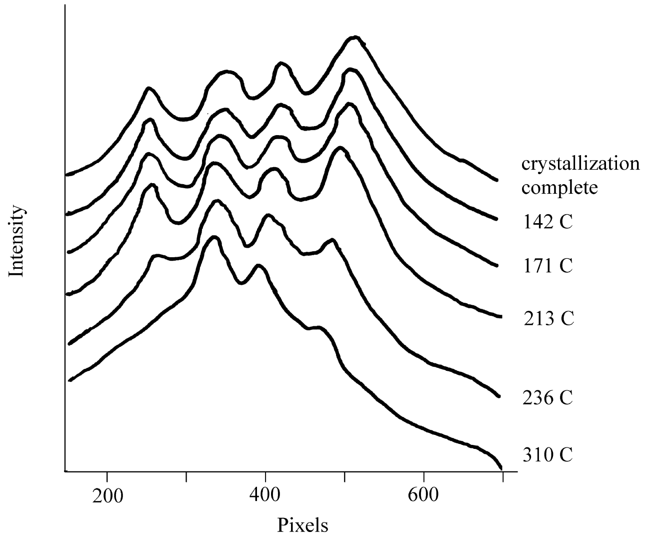

Fig. 11. Time-resolved WAXD pattern of PETA$_{25}$, cooled down from 310°C at 10°C/min to 150°C. Upper curve of PETA$_{25}$, when crystallisation is complete, after annealing at 150°C for 15 min. Temperatures in °C.

Fig. 11 shows the development of the WAXD patterns of PETA$_{25}$ during cooling from the melt (310°C), at this temperature, two peaks and a shoulder are clearly visible, on decreasing the temperature, two strong outer peaks appear. The two central peaks are clearly derived from the diamide, the crystalline form being present at 310°C. The ester segments crystallise later than the amide segments, and therefore the ester peaks develop later in the crystallisation process of PETA$_{25}$.

In the nucleation of PET by diamide segments, there seem to be two regions, depending on the diamide concentration. At low diamide concentrations, the presence of diamide segments in a polyester chain increases the interactions between those chains and reduces the entropy effect during crystallisation. It is expected that the diamide segments are already assembled in the melt and it is unlikely that the diamide segments crystallise before the ester segments as their crystallisation temperature is too low [16]. At a high diamide concentration in PET, the diamides are able to form a small amount of alternating amide–ester–amide segments, these have a high melting temperature. In PETA$_{25,}$ these crystalline segments were still present at 310°C and resulted in an increase in the crystallisation rate of PET. These amide–ester–amide segments are probably forming the nucleation sites.

4. Conclusions

The crystallisation rate of PET can be increased by incorporation of a low amount (2 mol%) of diamide segments, such as T2T, T4T and TϕT. Of these segments T2T is the most effective in nucleating PET, probably as it has approximately the same length and structure as the repeating unit of PET, and thus has a good fit in the PET crystalline lattice.

By using a zinc/antimony catalyst system instead of a titanium catalyst, a higher molecular weight of PETA can be obtained, resulting in the polymer having better properties. By incorporating diamide segments of a uniform length based on nylon 2,T (T2T) into PET, the glass transition, crystallisation and melting temperatures were all increased. Only one T_g of PETA was observed, thus indicating the presence of a homogeneous amorphous phase, the T_g was found to increase linearly with an increasing amide content. The T_{fl} was also increased with incorporation of diamide segments. PETA has a considerably higher dimensional stability then PET, with the water absorption being only slightly increased by the incorporation of amide segments. This suggests that both the crystalline and the amorphous phases are fairly inaccessible to water molecules under these conditions (20°C, 100% RH).

The crystallisation rate of PET is improved by incorporation of T2T segments. Small amounts (0.1 mol%) already enhance the rate of crystallisation. At higher amide concentrations, the crystallisation rate is further increased. Using time-resolved WAXD measurements of $PETA_{25}$ at 310°C, this being well above the melting temperature according to DSC, some sharp peaks were visible at the top of a broad peak, these sharp peaks corresponding to the crystalline amide segments. The sharp peaks that correspond to crystalline ester segments started to develop at lower temperatures. The hypothesis is that at higher amide concentrations, small alternating segments are present in the polymer chain (amide–ester–amide segments), which are expected to have a much higher melting temperature. Therefore, these may be present in the crystalline form at temperatures above the melting temperature of the polymer, and thus are able to act as crystallisation nuclei for PETA.

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