

# Segmented copolymers of poly(phenylene ether) and polyester

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## Abstract

Copolymers of telechelic poly(2,6-dimethyl-1,4-phenylene ether) (PPE) segments with terephthalic methyl ester end groups (PPE-2T, 3500 g/mol) and poly(dodecane terephthalate) (PDDT) were made via a polycondensation reaction in the melt. The inherent viscosities of the segmented copolymers were high. The thermal properties of the copolymers were studied by DMA. The segmented block copolymers had a transparent melt at low (12 wt%) PDDT contents. The segmented block copolymers had at higher PDDT contents a non-transparent melt and two glass transition temperatures. The glass transition temperature of the PPE phase decreased strongly with PDDT content in the copolymer. The glass transition temperature of the PDDT phase increased moderately with PPE content. At low PPE contents the modulus of the PDDT increased strongly with increasing PPE content.

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## 1. Introduction

Poly(2,6-dimethyl-1,4-phenylene ether) (PPE) [1–3] is a linear amorphous polymer with a high glass temperature of approximately 215 °C [4]. PPE has excellent properties such as high toughness, high dimensional stability, good flame retardation and low moisture uptake. However, due to its high glass transition temperature, very high processing temperatures are required, which can lead to thermal degradation. By lowering the  $T_g$  of the polymer, the processing temperature can be lowered and degradation free processing becomes possible. The  $T_g$  of PPE can be lowered by blending with polystyrene, as PPE and PS are fully miscible. The miscibility of PPE with other polymer systems like polyesters is low and the  $T_g$  of the PPE is not significantly lowered [1–3].

However, telechelic PPE segments are miscible with diols and with this system high molecular weight copolymers based on PPE could be made that have a

reduced  $T_g$  [5]. The telechelic PPE is made from high molecular weight PPE by a redistribution reaction [5–7]. The telechelic PPE was endcapped with terephthalic groups (PPE-2T) and had an average molecular weight of about 3500 [6]. The copolymers consist of PPE segments, which are extended by diester units. The copolymers had with diols one  $T_g$  and this  $T_g$  is decreased in temperature with increasing length of the diol [5]. If telechelic polyether segments were used like poly(tetramethylene oxide) with molecular weights ranging from 1000–2900 g/mol, the copolymers had two  $T_g$ 's and a reduced modulus at room temperature [5]. The miscibility of telechelic PPE-2T 3500 g/mol and diols is good but with PTMO segments with a molecular weight larger than 1000 g/mol poor. The diester segments do not crystallize as their melting temperature due to their small size is well below the glass transition temperature of the copolymer.

In the present work, segmented block copolymers are studied based on telechelic PPE and in situ prepared poly(dodecane terephthalate) segments (PDDT). The average length of the PDDT segments was varied changing the monomer feed composition. The starting materials are telechelic PPE-2T, dodecanediol and dimethyl terephthalate (DMT) are miscible. The dynamic mechanical behaviour is studied.

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## 2. Experimental

### 2.1. Materials

Dimethyl terephthalate (DMT), 1,12-dodecanediol (DDO) and toluene were purchased from Merck. Tetraisopropyl orthotitanate ( $\text{Ti}(\text{i-OC}_3\text{H}_7)_4$ ), obtained from Merck, was diluted in anhydrous *m*-xylene (0.05 M), obtained from Fluka. PPO-803<sup>®</sup> (11.000 g/mol) was obtained from GE Plastics (The Netherlands). All chemicals were used as received. PPE endcapped with terephthalic ester groups (PPE-2T) with an average molecular weight of 3700 g/mol (480  $\mu\text{mol OCH}_3/\text{g}$ , functionality = 1.79) and a bimodal molecular weight distribution was made in a two-step reaction as was described before [6]. This PPE-2T contained some unreactive high molecular weight PPE.

### 2.2. Synthesis of PPE-PDDT segmented block copolymers

The PPE-PDDT copolymers were synthesised by an ester type polycondensation reaction using PPE endcapped with terephthalic ester groups (PPE-2T), dodecane diol (DDO) and DMT. The preparation of a copolymer of PPE-2T (3700 g/mol) and PDDT with  $x=4$  is given as an example.

The reaction was carried out in a 50 ml glass reactor with a nitrogen inlet and mechanical stirrer. The vessel was loaded with PPE-2T (10.0 g, 4.8 mmol  $\text{OCH}_3$ ), DDO (94 g, 9.6 mmol), DMT (1.40 g, 7.2 mmol), 10 ml toluene and catalyst solution (0.5 ml of 0.05 M  $\text{Ti}(\text{i-OC}_3\text{H}_7)_4$  in *m*-xylene). This mixture was first heated in an oil bath to 120 °C under nitrogen flow. After 30 min the temperature was increased in steps: 30 min at 180 °C, 30 min at 220 °C and 60 min at 250 °C. The pressure was then reduced slightly ( $P < 20$  mbar) for 30 min and then further reduced ( $P < 1$  mbar) for 30 min. Finally, the vessel was allowed to slowly cool to room temperature whilst maintaining the low pressure. Then the polymer was cut out of the reactor and grinded in powder.

### 2.3. NMR

The composition of the copolymers were studied by <sup>1</sup>H NMR. The spectra were recorded on a Bruker spectrometer at 300 MHz and  $\text{CDCl}_3$  was used as a solvent. The PPE units have two aromatic protons with a peak at 6.466 ppm and side peaks at 6.692 and 7.35 [5]. The terephthalic group has four aromatic protons and with a peak at 8.087 ppm for PDDT and four peaks at 8.150, 8.178, 8.257 and 8.283 ppm for the terephthalate groups attached to the PPE.

From the peak intensities the concentration of the PDDT (including the terephthalic groups attached to the PPE) was calculated. The PDDT segment length can be calculated from the peak intensities of the PDDT units and the terephthalic groups attached to the PPE. The segment molecular weight was obtained by multiplying the segment length with the repeat molecular weight.

### 2.4. Viscometry

As an indication for the molecular weight, the inherent viscosity of the polymers was determined with a capillary Ubbelohde type 0C at 25 °C, using a polymer solution with a concentration of 0.1 g/dl in chloroform.

### 2.5. DMA

Samples for the DMA test ( $70 \times 9 \times 2$  mm<sup>3</sup>) were prepared on an Arburg-H manual injection moulding machine. Before use, the samples were dried in a vacuum oven at 80 °C overnight. The torsion behaviour was studied at a frequency of 1 Hz, a strain of 0.1% and a heating rate of 1 °C/min using a Myrenne ATM3 torsion pendulum. The storage modulus  $G'$  and loss modulus  $G''$  were measured as a function of temperature starting at –100 °C. The glass transition temperature ( $T_g$ ) was expressed as the temperature at which the loss modulus  $G''$  has a maximum. This maximum was 0–10 °C lower than the actual glass transition temperature, because with this DMA apparatus it was not possible to measure a few points around the  $T_g$  due to the very strong damping. The flow temperature ( $T_{\text{flow}}$ ) was determined as the temperature where the storage modulus  $G'$  reached 1 MPa.

## 3. Results and discussion

### 3.1. Introduction

The segmented block copolymers PPE-PDDT were synthesized from PPE-2T, DDO and DMT by a polyester condensation method (Fig. 1). The length of the PPE segment was 3700 g/mol and the length of the PDDT segment was varied by changing the monomer feed composition. The PPE-2T starting material also contained some high molecular weight unreactive PPE (6).

The PPE used for the distribution reaction was an industrial polymer (PPO-803<sup>®</sup>) with a number average molecular weight of 11.000 g/mol and inherent viscosity of 0.37 dl/g. All copolymers could be easily synthesized with inherent viscosities at least as high as the high molecular weight PPE (PPO-803<sup>®</sup>). The results on PPE-PDDT copolymers are summarized in Table 1. The results are discussed in two sections at high PPE contents (> 50 wt%) and at high PDDT contents (> 50 wt%).

The PDDT content in the copolymers as measured by NMR compared well with the starting composition of the reaction mixture. The PPE content is one minus the PDDT content. The starting mixture composition was used in the further analysis.

### 3.2. High PPE content

Copolymers with a high PPE content (> 50 wt%) were

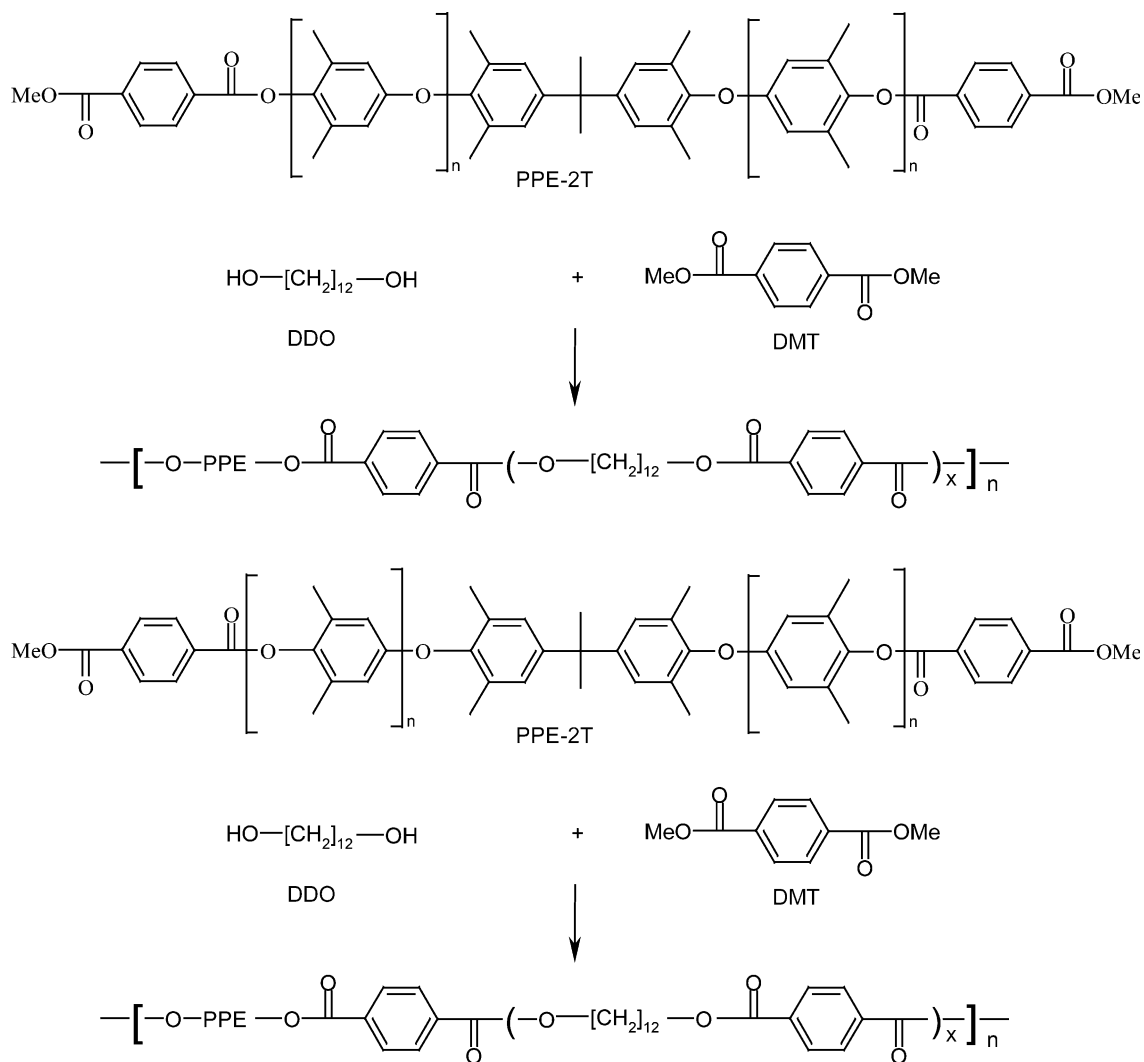


Fig. 1. Synthesis of the PPE-PDDT segmented block copolymer from PPE-2T, dodecanediol and dimethyl terephthalate.

Table 1  
Properties of the PPE-PDDT copolymers

	PDDT (wt%)	PDDT NMR (wt%)	$x^a$	PDDT length (g/mol)	$\eta_{inh}$ (dl/g)	$T_g$ PPE <sup>b</sup> (°C)	$T_g$ PDDT <sup>b</sup> (°C)	$T_{flow}$ (°C)
Starting materials								
PPO-803 <sup>®</sup>	–	–	–	–	0.37	200	–	222
PPE-2T <sup>c</sup>	–	–	–	–	0.19	173 <sup>d</sup>	–	–
PPE-2T/C12/DMT copolymers								
PPE-2T-DDO	12	13	1.2	560	0.33	170	–	195
PPE-PDDT	18	19	2.5	1000	0.70	155	–	208
PPE-PDDT	24	24	4.0	1500	0.56	144	85	197
PPE-PDDT	28	–	–	–	0.65	124	45	183
PPE-PDDT	36	37	8.4	3000	0.58	94	35	144
PPE-PDDT	48	49	11.8	4100	0.59	84	30	123
PPE-PDDT	73	–	–	–	0.65	–	9	128
PDDT	100	100	–	–	0.72	–	0	123

<sup>a</sup>  $x$  is the average number of repeating units in the PDDT segment as indicated in Fig. 1.

<sup>b</sup> Both the  $T_g$  of the PPE (rich) phase and the PDDT (rich) phase are given when a two-phase morphology is present.

<sup>c</sup> Made by two-step synthesis, bimodal,  $M_n \sim 3700$  g/mol [6].

<sup>d</sup> Measured by DSC instead of DMA.

made to study the effect of the PDDT length on the  $T_g$  of PPE and the phase separation (Table 1 and Fig. 2).

PPE (PPO-803<sup>®</sup>) is an amorphous polymer and has a high and sharp  $T_g$  of 200 °C (maximum of  $G''$ ) and a high and constant modulus up to the  $T_g$  and a flow temperature  $T_{flow}$  of 222 °C. This is a transparent single phase material. The PDDT is a typical semi-crystalline polymer with an amorphous and a crystalline phase and has a  $T_g$  at 0 °C and a flow temperature (melting temperature) at 123 °C. In the PPE-PDDT segmented block copolymers the  $T_g$  and  $T_{flow}$  decreases with PDDT content.

The PPE-PDDT with 12 wt% PDDT ( $x=1.2$ ), has a high and constant modulus, up to the sharp  $T_g$  at 170 °C [5]. This copolymer is a transparent material and has a  $T_g$  that is 30 °C lower than that of pure PPE. This suggests that this copolymer is a single phase material.

The incorporation of little more PDDT ( $x=2.5$ , 18 wt%) in the copolymer results a broadening and a lowering of the glass transition temperature (Fig. 1(b)) and the  $T_{flow}$  is also lower (Fig. 1(a)). The modulus is high up to the  $T_g$ . However, transparency is lost, indicating the presence of light-scattering domains.

When the PDDT content is increased to 24 wt% ( $x=4$ ,

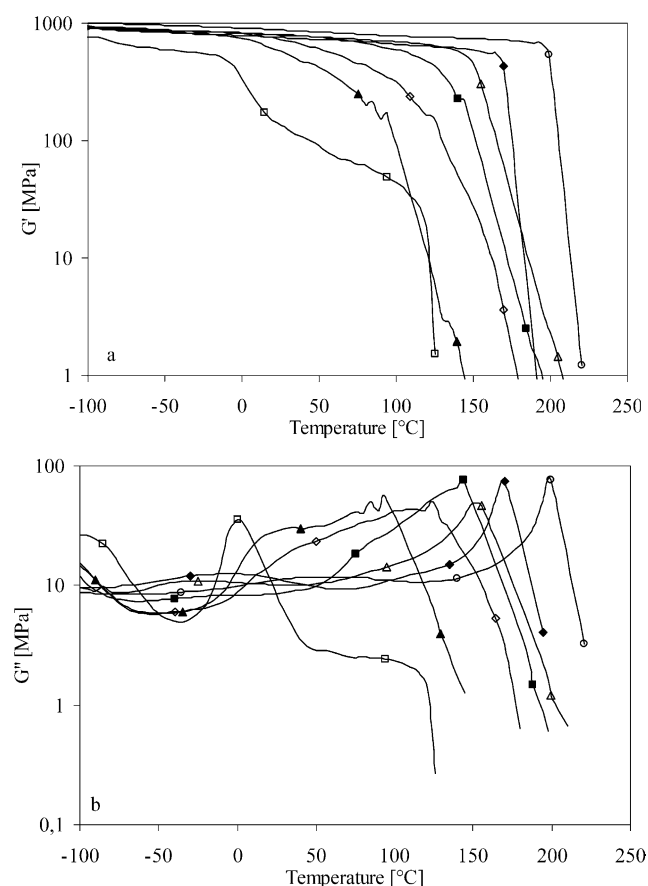


Fig. 2. Storage (a) and loss (b) modulus of PPE/PDDT copolymers with an average PPE length of  $\sim 3700$  g/mol and different PDDT contents: (○), PPE (PPO-803<sup>®</sup>); (◆), 12 wt% PDDT ( $x=1$ ); (△), 18 wt% PDDT; (■), 24 wt% PDDT; (◇), 28 wt% PDDT; (▲), 36 wt% PDDT; (□), PDDT.

segment length 1500 g/mol) the  $G''$  spectrum is further broadened. Next to a  $T_g$  for the PPE phase at 144 °C also a second transition at 85 °C is apparent. The modulus decreases now from the lower transition temperature.

When the PDDT content is increased further (28–36 wt% PDDT), the  $G''$  is strongly broadened and both the  $T_g$  for the PPE phase and the temperature of the lower transition are lowered. The modulus of these copolymers shows a substantial decrease starting at the lower transition temperature. This lower transition is not from a crystalline PDDT phase as the temperature of this transition is lowered with increasing PDDT segment length. This lower transition is from the amorphous PDDT phase containing some PPE segments. Thus two  $T_g$  are apparent from two amorphous phases. These segmented block copolymers are expected to have liquid-liquid demixed morphologies. As these segmented block copolymers have short segment length the phase size are expected to be small, but large enough to scatter light.

For these copolymers the  $T_g$ 's of the PPE rich and the PDDT rich phase are given as a function of the PDDT content (Fig. 3).

Both the  $T_g$  of the PPE rich phase and PDDT rich phase decrease with increasing PDDT content. The  $T_g$  of a fully miscible PPE-PDDT system can be modelled with the Fox relationship [8] (the dashed line in Fig. 3). The  $T_g$  decrease of the PPE phase follows the Fox relationship quite well. This suggests that the composition of the PPE phase is nearly similar to the composition of the block copolymer. However, the presence of a PDDT phase at PDDT concentration higher than 20 wt% indicates that long PDDT and PPE segments are not fully miscible. The  $T_g$  of the PDDT phase also decreases with PDDT content, however, that phase contains more PDDT than calculated with the Fox relationship. Thus the PPE  $T_g$  decreases with PDDT content roughly according to the copolymer composition while a second phase is formed rich in PDDT. As judged from the loss modulus ( $G''$ ) peak

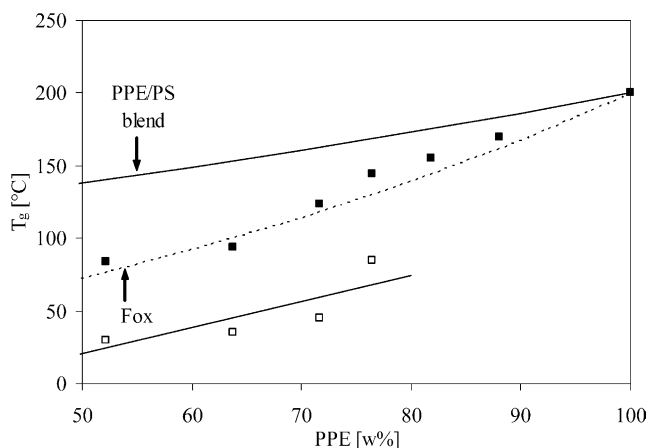


Fig. 3.  $T_g$  for PPE-PDDT segmented block copolymers as function of PPE content: (■), PPE rich phase; (□), PDDT rich phase. Also give is the  $T_g$  according to the Fox relationship [8] and the  $T_g$  of a PPE-PS blend.

intensities in Fig. 2(b) the concentration of the PDDT rich phase is small.

The segmented copolymer with 18 wt% PDDT is transparent and has one  $T_g$  at 155 °C. This copolymer can be compared with a PPE-PS blend (55–45) with a same  $T_g$ . In fact over the whole concentration range the PDDT is more effective in lowering the  $T_g$  of the PPE than PS (Fig. 3). Thus, the lowering of the PPE  $T_g$  is much more effective by copolymerisation with PDDT than by blending with polystyrene.

### 3.3. High PDDT content

PPE-PDDT copolymers with a high PDDT contents (>36 wt%) were studied as well. PDDT is a semi-crystalline polymer with a  $T_g$  at 0 °C and a  $T_m$  at 123 °C. The PPE can, if miscible, influence the  $T_g$ ,  $T_m$  and modulus above the  $T_g$  of PDDT. In Table 1 and Fig. 4 the DMA results for the copolymers with high PDDT contents are given.

When about 27 wt% PPE is incorporated in the PDDT polymer (73 wt% PDDT), the thermal behaviour as measured by DMA resembles that of the PDDT homopolymer. The

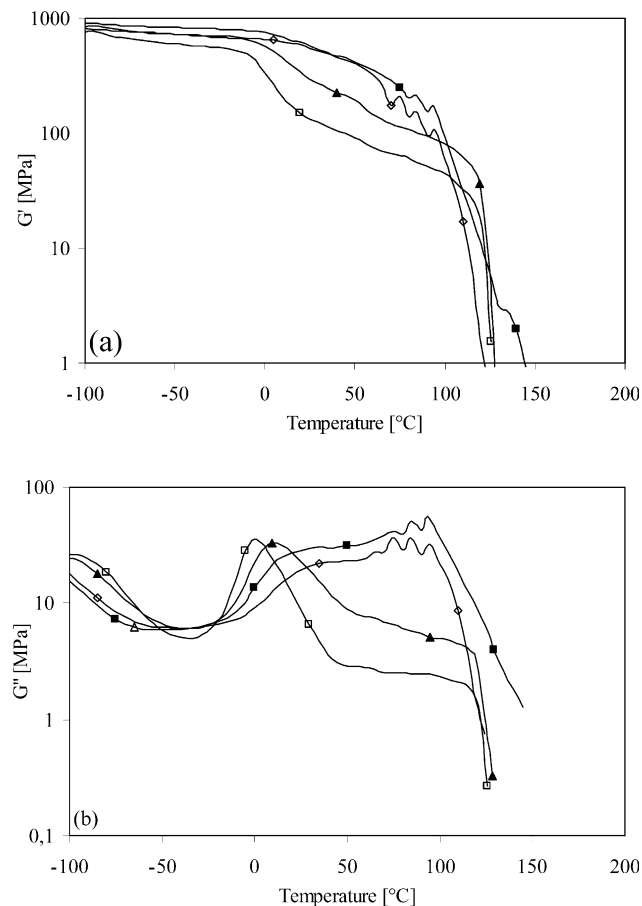


Fig. 4. Storage (a) and loss (b) modulus of PPE/PDDT copolymers with PPE of ~3500 g/mol and different PDDT contents: (■), 36 wt% PDDT; (◇), 48 wt% PDDT; (▲), 73 wt% PDDT; (□), PDDT.

copolymer has a  $T_g$ , a rubbery plateau and a sharp flow temperature. The glass transition temperature of the PDDT phase is increased by about 9 °C. This indicates that only about 5 wt% of PPE is mixed with the PDDT phase. The rest of the 27 wt% PPE is expected to have phase separated, but in the DMA-graph not even a broadening of the  $T_g$  is visible. The storage modulus for this copolymer in the  $T_g$ – $T_m$  region is increased, by a factor 2. This increase can be explained by the presence of these phase separated rigid PPE domains. The flow temperature of this PPE-PDDT segmented block copolymer is comparable with that of pure PDDT. The average PDDT segment length ( $x \sim 40$ ) (Table 1) is long enough to allow crystallisation.

In the PPE-PDDT copolymer with 52 wt% PPE the thermal behaviour is different from that of pure PDDT. The glass transition is now broad and consists of two transitions as in the PPE-PDDT copolymers with high PPE content. The first  $T_g$  is of PDDT rich phase and the second of a PPE rich phase. These two  $T_g$ 's have shifted compared to the homo polymers, which indicates that both phases are mixed phases. The  $T_{flow}$  of the copolymer is still at 123 °C. This flow temperature seems to be a combination of the PPE rich phase  $T_g$  and the PDDT melting temperature. Below the  $T_{flow}$  of this copolymer the storage modulus is relatively high. From this it is expected that the PDDT and PPE phases are co continuous.

The  $T_g$ 's and the  $T_{flow}$  of the high PDDT copolymers are given as a function of the PDDT content (Fig. 5). The  $T_g$  of the PDDT rich phase increases with decreasing PDDT (increasing PPE) content, however, this increase is less than expected from the Fox relationship [8]. This indicates that the PDDT rich phase contains little PPE and most of the PPE segments are, therefore, in separate amorphous domains. Up to 50 wt% PPE the PDDT phase seems to be semi-crystalline with a flow temperature between 120 and 130 °C and the PPE rich domains act as rigid modifier for the semi-crystalline PDDT.

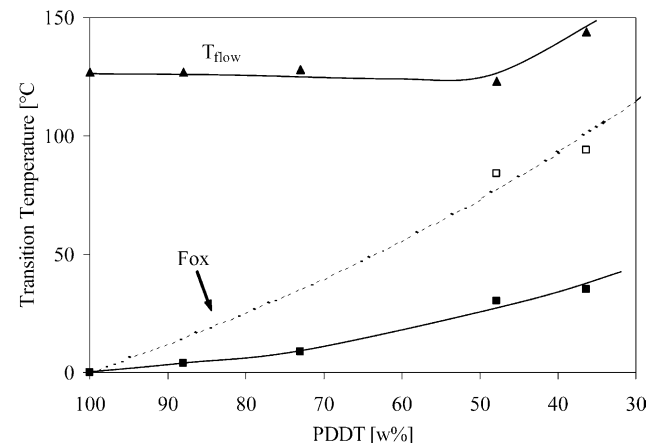


Fig. 5.  $T_g$  and  $T_{flow}$  for PDDT-PPE copolymers compared with the  $T_g$  of a (theoretical) blend of PPE with PDDT (according to the Fox relation) [8]: (■),  $T_g$  of PDDT rich phase; (□),  $T_g$  of PPE rich phase; (▲),  $T_{flow}$  of PDDT/PPE copolymer.

#### 4. Conclusions

The  $T_g$  and  $T_{flow}$  of the PPE-PDDT copolymers decrease with increasing PDDT length. However, at increasing PDDT length (above 1000 g/mol, PDDT content > 18 wt%) the  $T_g$  becomes broader and next to a PPE-rich phase also a PDDT-rich phase is formed. Only copolymers with very short PDDT ( $x=1.2$ ) are transparent and thus homogeneous on a micro scale. Copolymerisation is very effective in decreasing the  $T_g$  of PPE and, therefore, in lowering of the processing temperature.

The semi-crystalline PDDT has if copolymerized with 27 wt% PPE an increased  $T_g$  (9 °C) and an increased modulus. This  $T_g$  increase suggest that only 5% PPE is dissolved and thus the rest of the PPE is phase separated in separate domains. These rigid PPE domains act as reinforcing filler for the polyester and as a result the modulus above the  $T_g$  is increased by a factor 2. Possibly also other polyesters like PET and PBT can also be modified with PPE in this way.

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