Copolymers of PBT and Nylon 4T

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SYNOPSIS

Polybutylene terephthalate–nylon 4T copolymers (PBT–PA 4T) are synthesized from the diamide of diaminobutane and dimethyl terephthalate (DMT) with butane diol and more DMT in a concentration range of up to 50% PA 4T. The polymerization conditions were similar to those for PBT: first, a melt polymerization, followed by solid-state post-condensation. The materials were studied by differential scanning analysis (DSC) (melting and crystallization behavior) and dynamic mechanical thermal analysis (DMTA) (glass transitions and torsion moduli). The water absorptions were determined at 100% RH. By increasing the PA 4T content in the copolymers, melting temperatures increased strongly, heats of fusion decreased slightly, and glass transition temperatures increased linearly. The torsion moduli above the glass transition temperature were higher. © 1993 John Wiley & Sons, Inc.

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INTRODUCTION

Polybutylene terephthalate (PBT) is a very interesting engineering plastic. The polymer has a high structural regularity and, due to this, a high crystallinity and crystallization rate. Results of this are moduli above the glass transition temperature high and good solvent resistance. PBT is processable and has a low water absorption. A disadvantage of this polyester is its relatively low melting (220°C) and glass transition temperatures (45°C).

Modification by copolymerization, e.g., with amides, usually causes a lowering of the melting temperature and order. An exception is the regular alternating polyesteramides (PEA). These alternating PEA show thermal and mechanical behavior and have a unit cell structure typical of semicrystalline homopolymers.^{1–4} The most-studied alternating PEA is synthesized from 1,6-hexanediamine and 1,6-hexanediol with terephthalic acid (T6T6).^{2–6} T6T6 possesses physical properties comparable to those of polyethylene terephthalate; it has a T_m of 25°C, a T_g

of 49°C (66% RH), but the G modulus above T_g drops sharply.⁵ Williams synthesized its alternating PEA according to the following scheme²:

The T6T-dimethyl was made with the half acid chloride ester of dimethylterephthalate (DMT) and a diamine.⁸ Manzini⁶ made the T6T-dimethyl with excess DMT, the diamine, and Li(OCH₃) as a catalyst. Of the alternating PEA with short chain glycols (C₂–C₅) and short chain diamine (e.g., C₄) only polymers of very low molecular weight could be obtained. (This is probably due to competing side reactions.²)

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Randomization of PEA decreases the order of these systems and as a result, a lowering of the mechanical properties (e.g., moduli above their T_g).¹⁻³ In this article we report on the synthesis and properties of PEA synthesized from 1,4-butanediamine and 1,4-butanediol with DMT, which is a family of PBT copolymers.

EXPERIMENTAL

Materials

Dimethylterephthalate (DMT), 1,4-butanediamine (BDA), and 1,4-butanediol (BDO) were obtained from Merck. BDA and BDO were distilled prior to use.

The catalyst was a solution of 1.48 g tetraisopropyltitanate and 0.1 g Na in 30 mL of distilled *n*-butanol.

N, N'-bis(*p*-carbomethoxybenzoyl)butanediamine (T4T-dimethyl)^{6,9} was synthesized through the following procedure: 111 g (0.6 mol) DMT, 5 g (0.06 mol) BDA, 395 mL anhydrous toluene, 106 mL of anhydrous methanol, and 10 mL Li(OCH₃) (1.89 *M* in methanol) were mixed in a flask with a stirrer, condenser, and nitrogen inlet. The flask was heated to reflux for 40 h. During this time the reaction product precipitated. The precipitate was separated by hot filtration, washed twice with hot toluene and once with hot methanol, and was subsequently dried (24 h at 100°C).

Polymer Synthesis

The PEAs studied have amide concentrations of 0–50 mol % and are denoted PEA 0–50.

Prepolymerization

The reactions were carried out in a 250 mL glass vessel with a nitrogen inlet and mechanical stirrer. A typical example of a synthesis of a 25 mol % amide sample (PEA-25) is given below; 10.0 g T4T-dimethyl (24.3 mmol), 9.46 g DMT (48.7 mmol), 13.1 g BDO (145.5 mmol), and 0.4 mL catalyst solution was reacted for 30 min at 180°C. After this the temperature was raised to 250°C and vacuum applied (10–15 mm Hg) for 30 min. Subsequently the tem-

perature was further increased to 265°C and the pressure reduced to 0.1–0.01 mm Hg and the reaction was kept at those conditions for 1 h.

Postcondensation

The prepolymer materials were grounded and postcondensed in the solid state, 24 h at 200–230°C in a stream of nitrogen.

Characterization

The η_{inh} of the PEA-0–35 was measured at 25°C using a 0.25% solution in PhOH/C₂Cl₄H₂ (50/50 mol %). For PEA-40 and -50 a 0.5% solution in 96% H₂SO₄ was used with a constant solution time of 6 h.

Thermal Analysis

Differential scanning calorimetry (DSC) (Perkin-Elmer DSC-4) was used with a heating and cooling rate of 20°C/min. The melt-pressed samples were first heated to 20°C above their melting temperatures (T_{m1} , ΔH_{m1}), cooled (T_c), and heated again (T_{m2} , ΔH_{m2}). The area under the melting curve was used as the heat of fusion, the peak maximum as the melting temperature.

Water Absorption at 100% RH

A melt-pressed sample was first dried in a vacuum oven (24 h at 100°C) and weighed. After the water absorption the sample was weighed again. Two methods were used: (method 1) the sample was suspended in boiling water for 24 h, and (method 2) the sample was kept in a desiccator above water at 20°C for 1 month.

Dynamic Mechanical Analysis

With a Myrenne (ATM 3) torsion pendulum instrument the torsion moduli G' and G'' were analyzed at a constant frequency of 1 Hz and a heating rate of 1°C/min.

RESULTS AND DISCUSSION

Synthesis

The PBT copolymers with BDA were prepared with the "T4T-dimethyl." The T4T-dimethyl was synthesized from BDA and a large excess of DMT in a methanol/toluene mixture at reflux temperature.⁶

Figure 1. IR diagram of T4T-dimethyl.

Soon a suspension was formed of the monoamide which was slowly converted to the T4T-dimethyl. As a catalyst LiOCH_3 was added (and this also avoids salt formation). With IR spectroscopy, the formation of amide groups could be observed and in the T4T-dimethyl the amide carbonyl band (1640 cm^{-1}) was as strong as the ester carbonyl band (1720 cm^{-1}) (Fig. 1). The T4T-dimethyl has a melting point of 257°C and a heat of fusion of 144 J/g .

Prepolymer

The first stage of the reaction is a transesterification step during which the methyl esters of DMT and

the T4T-dimethyl are replaced by butyl esters of BDO. After this step the temperature is raised and vacuum is applied.

This polycondensation step is carried out in two stages: first at 250°C and a moderate vacuum (20 mbar) and then at 265°C and high vacuum conditions (0.1 mbar). The influence of the transesterification conditions were studied on PEA-25. In order to prevent cyclization of butanediol the transesterification reactions were carried out at 200°C or lower temperatures. The lower limit is formed by the ability of DMT and BDO to keep the reaction mixture liquid. The results of these reactions are given in Table I. The effect of reaction temperature (170–

Table I. Prepolymerization Conditions: PEA-25 (25% Amide)

No.	Transesterification		Polycondensation (1 h at 265°C)	
	T ($^\circ\text{C}$)	t (min)	P (mmHg)	η_{inh} (dL/g)
1	200	45	0.1–0.01	0.69
2	180	45	0.03–0.01	0.83
3	180	30	0.05–0.01	0.94
4	180	30	0.05–0.01	0.74
5	180	20	0.02–0.01	0.85
6	180	20	0.02–0.01	0.78
7	170	30	0.03–0.01	0.78

Table II. Postcondensation Reactions: PEA-25 (25% Amide), 24 h Nitrogen Atmosphere

No.	Reaction Temperature (°C)	η_{inh} (dL/g)
1	—	0.83
1A	220	1.29
1B	230	1.03
2	—	0.85
2A	200	1.23
2B	210	1.13
2C	220	1.30
3	—	0.94
3A	230	1.19
3B	240	1.13

200°C) and time (20–45 min) is small, but it seems that with a transesterification temperature of 170–180°C somewhat higher viscosities of the prepolymer were obtained.

Postcondensation

High molecular weight polyesters are usually obtained by postcondensation in the solid state at 10–20°C below the melting temperature.¹⁰ The results of some postcondensation reactions of PEA-25 are given in Table II. The best results were obtained by a solid-state postcondensation of PEA-25 in the region 200–220°C.

Amide Content Variation

PEAs were synthesized with varying amounts of amide. If the amount of the high melting T4T-dimethyl is increased, it will become more difficult to

Figure 2. Melting temperatures: (■) first and (●) second run.

keep the reaction mixture liquid during the transesterification step. These reactions (PEA-35–50) are carried out at 190°C with a larger excess of BDO.

The results of the reactions with different copolymers compositions are listed in Table III. The viscosities of the PEA decreased with increasing amide content. The reason for this is as yet unknown.

DSC

The melt-pressed polymers were scanned to 20°C above their melting points, cooled at 20°C/min, and scanned again at 20°C/min. The observed melting transitions and heats of fusion are given in Table III and Figures 2 and 3.

There were hardly any differences between T_{m1} and T_{m2} of the melt-pressed samples. The melting

Table III. Properties of PEAs

No.	PEA (Amide %)	η_{inh} (dL/g)	$T_{m,1}$ (°C)	T_c (°C)	$T_{m,2}$ (°C)	$\Delta H_{m,1}$ (J/g)	$\Delta H_{m,2}$ (J/g)	$T_{g,dry}$ (°C)	$T_{g,wet}$ (°C)
ind. ^a	0	1.01	224	177	224	52	50	50	—
8	0	1.66	223	190	222	44	43	47	40
9	10	1.32	232	201	232	47	53	59	40
10	20	—	—	216	244	—	44	—	—
11	25	1.19	264	236	261	42	41	78	48
12	30	0.51	—	227	268	—	47	85	—
13	35	0.31	289	255	286	39	27	88	48
14	40	— ^b	316	—	—	23	—	116	44
15	50	0.43	382	—	—	42	—	110	—
4,T ^c	100	0.19	428/475	—	—	108	—	—	—

^a Arnite KN 159904.

^b Did not dissolve completely.

^c Reference 11, cast film.

Figure 3. Heats of fusion: (■) first and (●) second run.

temperatures increase with amide content without showing the usual melting point depression of copolymers. The difference between the crystallization temperature (T_c) and the second melting temperature ($T_{m,2}$) remains almost constant.

There was a considerable spread of values of the heats of fusion (ΔH_m), but the overall trend is that there is only a slight decrease with increasing amide content compared with the PBT homopolymer. This means that we are dealing with copolymers which are nearly as highly ordered as PBT and which crystallize as fast as PBT.

Mechanical Properties

The torsion properties were studied on melt-pressed strips, dried, and conditioned at 100% RH. The glass transition (G''_{max}) was in all cases a single transition (Fig. 4) and the glass transition temperatures increased linearly with the amide content (Fig. 5, Table III). This effect was much stronger for the dry samples than for the wet samples. The copolymers kept their G' above their T_g remarkably well (Fig. 4) up to a factor of 2 better than the PBT and sustained high moduli to appreciably higher temperatures. The high torsion moduli above T_g also suggest that these PEA copolymers have a high degree of order.

Figure 4. Dynamic mechanical analysis, G' and G'' : (—) PBT, (---) PEA-10, (· · · · ·) PEA-25, (- - -) PEA-30, (- - - -) PEA-35, (- · - · -) PEA-40, (- · - -) PEA-50.

Water Absorption

The water absorption at 100% RH of the copolymers increases ascentotial with increasing amide content (Fig. 6). The water absorption of the boiled up samples is slightly higher than for samples conditioned at RT. Up to PEA-25 the water absorption increase is small.

Solubility

PEA proved to be insoluble in almost every solvent. In the PBT solvent PhOH/C₂Cl₄H₂ PEA-0-35 only dissolved at higher temperatures and PEA-40-50 not at all. PEA is soluble in H₂SO₄ but this solvent degrades the polymers.

CONCLUSIONS

PBT has a high order but not so high melting (220°C) and glass transition temperatures (45°C). Nylon 4, T has a high order similar to PBT with, however, a very high melting temperature (425/475°C), which is too high for melt processing.¹¹ Copolymers of PBT and nylon 4, T were synthesized by first making a T4T-dimethyl. Starting with this T4T-dimethyl the synthesis of the copolyesteramides is similar to that of PBT. The molecular weights of the copolymers were found to decrease with amide concentration.

As expected, the T_g , as well as the T_m and the torsion moduli, increased with amide concentration, at higher temperatures. The order and the rate of crystallization in these copolymers remained high. The water absorption increased but stayed reason-

Figure 5. Glass transition temperatures: dry (■) and at 100% RH (●).

Figure 6. Water absorption at 100% RH. Conditions: (■) 24 h at 100°C, (●) 1 month at 20°C.

ably low up to PEA-25 and the solvent resistance improved.

Thus, it is possible to modify PBT with 1,4-butanedi-amine to copolymers with not only higher glass transition temperatures but also higher melting temperatures and better mechanical properties.

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