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Polyesters with Enhanced Heat Resistance. Plastics and Fibres

Abstract
Dimethyl terephthalate (DMT) and dimethyl 2,6-naphthalate (DMN) copolymers with ethylene glycol (EG) were obtained by the melt polycondensation method. Melt points and glass transition temperatures were determined for selected copolymers using DSC. The evaluation of their thermal stability was based on TGA results. Changes in relative viscosities and the lowering of the mass of the polymer samples after long-lasting heating at 200°C as well as changes in the melt viscosity after 1 h of heating at 290°C were also investigated. Fire resistance was evaluated on the basis of the oxygen index (OI) tests. The mechanical properties and thermal stability of fibres obtained from DMT/DMN copolyesters were also determined.

Key words: *dimethyl terephthalate, dimethyl 2,6-naphthalate, thermoresistant polyesters, thermoresistant fibres.*

■ Introduction

For many years thermo and fire-resistant modified polyesters have been the subject of numerous studies all over the world. In these studies, dimethyl terephthalate (DMT) and ethylene glycol (EG) are very often used as the initial materials in the synthesis of poly(ethylene terephthalate) (PET).

PET can be considered as a material with moderate flammability, good thermal stability, and advantageous mechanical properties. However, it is possible to impro-ve its properties by the incorporation of highly aromatised sequences [1,2] into their macromolecular chains.

The aim of this work was to obtain copolyesters characterised by better thermal and flame resistance than PET alone. Therefore, the studies focused on the synthesis and characterisation of the resulting copolyesters from DMT, dimethyl 2,6-naphthalate (DMN) and EG. It is known that the poly(ethylene 2,6-naphthalate) (PEN) polymer (obtained from DMN and EG) has a higher thermal stability and mechanical resistance than PET [3,4].

Thus, it can be expected that the composition of a copolyester will affect its properties, and the increase of the content of DMN in it should improve the thermal and flame properties of the copolymer.

The aim of this study was to improve the thermal stability of PET by the incorporation of higher aromatic segments into the polymer chains. In our work we partially replaced DMT by DMN in the initial mixture of monomers.

■ Experimental

Materials
■ Dimethyl ester of terephthalic acid (DMT), manufactured in "Elana" Toruń, Poland.
■ Dimethyl ester of 2,6-naphthalenedicarboxylic acid (DMN), Amoco, Belgium.
■ Ethylene glycol (EG), Orlen, Poland.
■ Manganate acetate, India.
■ Antimony trioxide, Japan.
■ Glycol ester of phosphoric acid (GEPA), trade name - Argoflan, Poland.
All the reagents mentioned above were used without purification.

Syntheses of copolyesters
The preliminary experiments of the synthesis of copolyesters were carried out in a 0.9 dm^3 reactor constructed at the Institute of Chemical Fibres and used for obtaining polyesters by the melt polycondensation method.

The syntheses of DMT/DMN copolyesters selected for the fibre spinning were performed in a 30 dm^3 reactor made by Fourne (Germany).The synthesis was carried out in two stages. At the stage of the ester exchange (first stage), the comonomers (DMT and DMN) were reacted with ethylene glycol to form β,β'-bishydroxyethylene terephthalate (1) and 2,6-dihydroxyethylenenaphthalate (2). As a catalyst, manganate acetate (0.04 wt.%) (acidic component) was applied. The ester exchange process was carried out at temperatures ranging from 185 to 225°C with the evolution of methyl alcohol. The polycondensation (second stage) of the obtained esters 1 and 2 was carried out at 285-300°C under the pressure of 1 hPa, until the determined viscosity of reaction mixture was reached.

GEPA in the amount of 0.04 wt.% of DMT was used as a stabiliser. The polycondensation process was catalysed by antimony trioxide Sb_2O_3/DMT=0.035 wt.%. The time of the reaction ranged from 40 to 100 min. The procedure of the synthesis was analogous to that described earlier [5-8].

Fibre formation
The spinning of filaments from DMT/DMN copolymers was carried out using a melt spinning machine (IWCh) equipped with an extruder (Barmag): D=20 mm L/D=20, using a spinning speed of
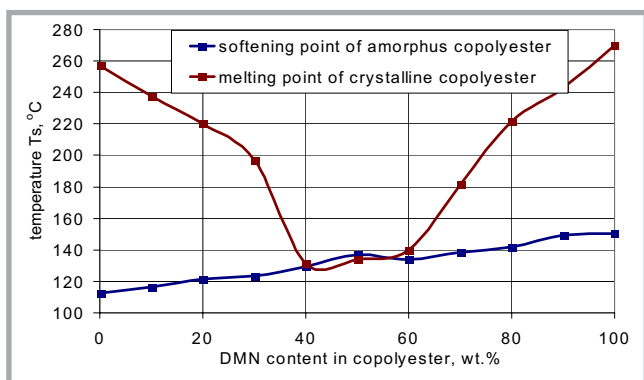
Figure 1. *Melting point and softening point of PET, PEN and DMT/DMN copolyesters.*
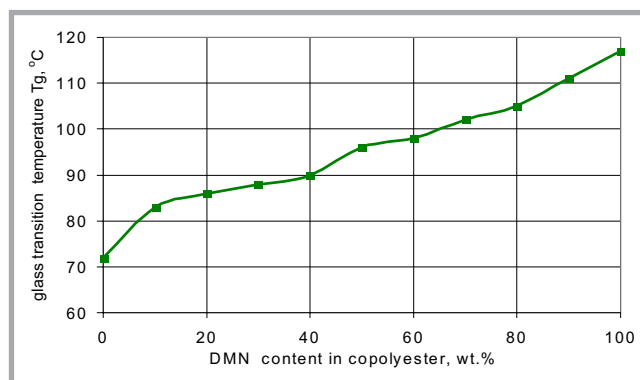

Figure 2. *Glass transition temperatures PET, PEN and DMT/DMN copolyesters.*

1000-1500 m/min. The applied temperature of the melt depended on the melt flow index (MFI) value measured in the temperature range from 285 to 305°C, selecting the temperature when the MFI was about 1 g/10 min.

The as-spun fibres were drawn on an SZ-16 draw-twist machine (Barmag) with a speed of 460 m/min. The temperature of the godet was adjusted within the range 85-125°C (5-10°C above T_g), and the temperature of the heating plate ranged from 145-160°C.

The draw ratio was chosen considering the remaining elongation within the range 2.47 to 4.41. For the selected draw ratio of ~4.3, trials of drawing were performed with an additional stabilisation (option 1), and the trials of additional stabilisation of filaments were carried out on the drawing machine (option 2). The temperatures of the heating plates during stabilisation depended on the kind of the copolyester used to manufacture the filaments (temperature of their softening), and in option 1 they ranged from 145 to 220°C, whereas in option 2 they ranged from 170 to 220°C.

Method of preparation of polymers for thermal stability tests

The polymers obtained in the polycondensation process were disintegrated in an impact-mill (Hitachi - Japan) cooled with liquid nitrogen. The fraction grain size of 0.2-0.75 mm was applied for the examination of thermal stability.

Methods of analysis

Thermal stability tests of polymers under investigation were carried out on a TGS-1 thermobalance (Perkin-Elmer). The heating rate was 10°C/min, and the nitrogen flow about 30 cm³/min.

Polymer powders were subjected to long-lasting heating (287 h) in air in a laboratory drier at 210 and 180°C. Then relative viscosity (η_{rel}) and weight change were determined. Relative viscosity was determined in an Ubbelohde viscometer with an IIA capillary k=0.01. The polymer concentration in phenol-tetrachloroethane solution (1:1 wt.) was 0.4 g/dm³. The measurements were carried out at 25°C.

The softening points of polymers were determined by a penetrometric method using the TSPA No 7-78 type apparatus (Townsend-Crowther Ltd, Hitchin, USA). The thermal properties of the polymer were evaluated by differential scanning calorimetry (DSC) using a Perkin-Elmer apparatus. The measurements were performed in the atmosphere of nitrogen with a heating and cooling rate of 20°C/min. The mass of the examined samples ranged from 5 to 15 mg. Registration sensitivity was 4-84 mJ/s.

The measurements of the MFI were carried out using a P/N 6941.000 CEAST Melt Flow Tester (the load was 2.16 kg, the spinneret ⌀ 0.5 mm, the temperature 290°C). The thermal stability of fibres was determined according to established procedure [9]. The samples, in the form of 100 m long filament hanks, were placed in a drier under an introductory load of 2.5 g and heated at 160°C for 24 and 72 h. After heating, the samples were conditioned for 24 h under the normal climate conditions (temperature 20°C±2°C, RH=65%±2%). The breaking force of

a single thread was determined according to established procedure [10]. The thermal stability of fibres Q was calculated from the following formula:

$$Q = \frac{P_1}{P} x\, 100\%$$

Q - thermal stability of fibre,
P_1 - breaking force of thread after heating,
P - breaking force of thread before heating.

The *OI* (oxygen index) value was determined according to the relevant standard [11], and calculated from the formula:

$$OI = \frac{[O_2]}{[O_2]+[N_2]} \cdot 100\%$$

where:

$[O_2]$ - the minimum oxygen amount in its mixture with nitrogen ensuring total burning of the sample (dm³/h);

$[N_2]$ - the nitrogen amount corresponding to the minimum oxygen amount (dm³/h).

■ Discussion

Synthesis and properties of DMT/DMN copolymers

Nine DMT/DMN copolyesters were obtained. The weight percentage of comonomers varied from 10 to 90%. For comparison, standard polymers PET and PEN were also prepared. The dependence of softening points (T_s) and glass transition temperatures (T_g) as a function of copolymers composition is shown in Figures 1 and 2 respectively.

Table 1. *Thermal properties of polymers based on TGA analysis.*

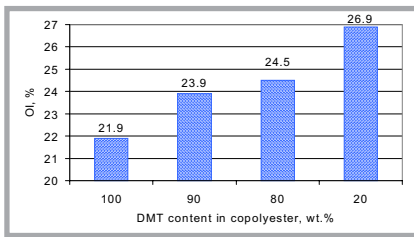| Composition of polymer	Temperature at which 5% decrease of weight occurs, °C
DMT 100 (PET)	417
DMN 100 (PEN)	430
DMT/DMN 80/20	424
DMT/DMN 20/80	429

Figure 3. OI value for PET and DMT/DMN copolyesters.

The copolymers have an irregular structure in comparison to the regular structure of PET and PEN homopolymers. This is manifested by lowering their softening temperatures and the significant decrease of their ability to crystallise. The results obtained agree with those described in the literature [12-14]. Standard PET crystallises at 140°C in 2 h, while crystallisation of PEN needs 20 h at the same temperature. The lowest ability to crystallisation was observed for copolymers when the weight ratio of DMT/DMN approaches 1. The higher content of DMN causes the increase in the T_g of copolymers. DMT/DMN copolymers have considerably lower softening and melting temperatures than PET.

For the thermal stability tests, two DMT/DMN copolymers (20/80 and 80/20) were selected. The copolymers with the compositions from 70/30 to 30/70 had a weak crystallisation ability and low melting temperatures.

The results of thermal stability tests carried out by the thermo-gravimetric method (TGA), for copolymers and homopolymers PET and PEN, are shown in Table 1. The increase in DMN content in any copolymer improves its thermal stability. The thermostability of the copolymers obtained is higher than the thermal stability of PET but lower than that of PEN.

Three samples of the copolyesters DMT/DMN (90/10, 80/20 and 20/80) in the form of powders were subjected to a thermal stability test by heating for 287 h at 205°C. The mass loss of these samples was determined and the relative viscosities before and after heating were measured. The melting temperatures obtained together with glass transition for these copolymers are given in Table 2.

As can be seen, the lowering of the relative viscosity resulting from heating the material is smaller, as the DMN content in the copolymer is higher. Such a dependence is not observed in the case of mass loss measurements.

The determination of the copolymer thermal stability was also performed using melt flow index (MFI) measurements. This parameter was examined after 6, 30, and 60 min of heating sample at 290°C. The results of these measurements are collected in Table 3. As seen in Table 3, the increase of the content of DMN in copolymers improves their thermal stability. Oxygen indices were determined for all analysed DMT/DMN copolymers, and the results obtained are presented in Figure 3. For the higher DMN content, higher OI values were observed.

Formation and properties of fibres from DMT/DMN copolymers

Fibre-forming PET (Elana) and selected DMT/DMN copolymers were used to obtain continuous fibres. The final product had a linear density of about 45 dtex and consisted of 17 filaments. The physico-mechanical properties and thermal stability of the fibres drawn and stabilised accor-

Table 2. Properties of DMT/DMN copolymers heated at 205°C for 287 h (Δm - mass change of the examined sample after heating, T_m - melting temperature).

Composition, wt.%		T_g, °C	T_m, °C	Δm, %	η_{rel} before heating	η_{rel} after heating	Viscosity change, %
DMT	DMN						
100	-	90	257	-1.99	1.294	1.205	-6.9
90	10	90	239	-1.60	1.278	1.240	-7.5
80	20	94	221	-1.81	1.280	1.227	-4.3
20	80	104	215	-1.21	1.247	1.207	-3.3

Table 3. Dependence of flow index from heating time (temperature 290°C, spinneret $\varnothing$=0.5 mm, load 2.16 kg).

Composition	MFI, g/10 min				
	after 6 min	after 30 min	change, %	after 60 min	change, %
PET (Elana)	1.61	1.82	13.0	2.13	32.3
DMT/DMN 90/10	1.93	2.19	13.5	2.50	29.5
DMT/DMN 80/20	1.19	1.32	10.9	1.50	26.0
DMT/DMN 20/80	0.95	1.02	7.4	1.14	20.0

Table 4. Selected properties of fibres from DMT/DMN copolymers drawn with stabilisation (option 1).

Processing stage	Property	Unit	Fibres			
			PET	DMT/DMN 90/10	DMT/DMN 80/20	DMT/DMN 20/80
Before heating	Draw ratio	-	4.23	4.38	4.5	4.23
	Linear density	dtex	47.4	45.7	44.7	47.8
	Breaking force P	cN	263	203	237	224
	Tenacity	cN/tex	55.4	44.4	52.9	46.9
	Elongation	%	18.8	19.6	17	15.1
After heating at 160 °C for 24 h	Breaking force P_1	cN	248	201	229	201
	P_1/P x 100%	-	94.3	99.0	96.6	89.7
After heating at 160 °C for 72 h	Breaking force P_2	cN	243	192	223	221
	P_2/P x 100%	-	92.4	94.6	94.1	98.7

Table 5. Selected properties of fibres from DMT/DMN copolymers stabilised after drawing (option 2).

Processing stage	Property	Unit	Fibres			
			PET	DMT/DMN 90/10	DMT/DMN 80/20	DMT/DMN 20/80
Before heating	Draw ratio	-	4.23	4.38	4.5	4.23
	Linear density	dtex	47.5	45.6	44.2	46.6
	Breaking force P	cN	261	224	219	196
	Tenacity	cN/tex	54.9	49.1	49.5	42.0
	Elongation	%	16.1	18.1	14.9	11.9
After heating at 160 °C for 24 h	Breaking force P_1	cN	247	222	218	186
	P_1/P x 100%	-	94.6	99.1	99.5	94.9
After heating at 160 °C for 72 h	Breaking force P_2	cN	212	201	211	186
	P_2/P x 100%	-	81.2	90.0	96.3	94.9

Table 6. *Results of calorimetric (DSC) determination for fibres from DMT/DMN copolymers after heating at 160°C. The fibres were drawn with stabilisation (T_m - melting temperature, T_c - crystallisation temperature from the melting stage, ΔH_m - melting enthalpy).*

Examined fibres		Heating		Cooling	
Composition DMT/DMN	Heating period	T_m	ΔH_m	T_c	T_g
wt.%	hours	°C	J/g	°C	°C
PET	0	256	58.7	218	-
	24	256	61.9	220	-
	72	260	62.3	219.5	-
DMT/DMN 90/10	0	240	50.2	173	-
	24	240	58.1	171	82
	72	240	57.4	172.5	82
DMT/DMN 80/20	0	220	37.1	-	82
	24	203	50.0	148	85
DMT/DMN 20/80	0	210	31.6	-	105
	24	211	42.9	-	106
	72	210.5	52.1	-	105

Table 7. *Results of calorimetric (DSC) determination for fibres from DMT/DMN copolymers after heating at 160°C. The fibres were drawn after them stabilised. (T_m - melting temperature, T_c - crystallisation temperature from the melting stage, ΔH_m - melting enthalpy).*

Examined fibres		Heating		Cooling	
Composition DMT/DMN	Heating period	T_m	ΔH_m	T_c	T_g
wt.%	hours	°C	J/g	°C	°C
DMT/DMN 20/80	0	210	33.4	-	104
	24	211	44.9	-	106
	72	212	41.9	-	106

ding to options 1 and 2 were evaluated. The results are presented in Tables 4 and 5.

The tensile strength of copolyester fibres was lower than for PET fibres alone. The analysis of the mechanical properties of fibres leads to the conclusion that drawing with stabilisation (Table 4) is a much better method of thermal treatment than thermal stabilisation after drawing (Table 5).

Copolyester fibres were also characterised by a higher thermal stability than PET fibres. After 72 h of heating, the breaking force of PET was lowered to 92.4% of its initial value for option 1 and to 81.2% for option 2, whereas for fibres from copolyester DMT/DMN 80/20, the same parameters were 98.7 and 94.9% respectively. DMT/DMN 20/80 fibres stabilised after drawing have different thermal stability than the remaining fibres. The fibres formed from DMT/DMN 20/80 copolymer after 24 h of heating at 160°C showed a decrease in strength, but further heating, even for 48 h, does not affect their mechanical characteristics. For all the other fibres, their tensile strengths gradually lowered with prolongated heating.

Tables 6 and 7 show the results of the determination of some thermal properties of fibres. The fibres drawn with stabilisation (option 1) have a higher degree of crystallisation as the result from heating. This can be proved by the increase of melting enthalpy (ΔH_m) values (a small deviation can only be observed for DMT/DMN 90/10 copolyester, after 24 h of heating ΔH_m= 58.1 J/g, and after 72 h ΔH_m=57.4 J/g). It is worth mentioning that the increase in fibre crystallinity causes the lowering of their tensile strength.

Complex structural phenomena are observed in fibres prepared from the DMT/DMN 20/80 copolymer. The crystallinity of fibres continuously grows during heating, while their tensile strength first decreases and then rises again. When heating fibres with identical composition but stabilised after heating (option 2), growth of their crystallinity in the first 24 h is observed. Further heating, however, leads to the decrease in crystallinity (after 72 h). The breaking force of the fibres, after the initial lowering, remains at a constant level. the optimisation of properties of these fibres needs further research into the conditions of their spinning and drawing.

In order to evaluate the changes resulting from the degradation and/or destruction occurring in the fibres during their heating, the relative viscosity of unheated and heated fibres at 160°C for 72 h was determined. After heating in the above conditions, PET and copolyester DMT/DMN 90/10 fibres showed an 0.8% decrease in viscosity, while for fibres from DMT/DMN 80/20 and 20/80 copolyesters, the relative viscosity remained at the same level. The above results of viscometric measurements showed that there are no changes in the degradation-destruction type of polymer structures after 72 h of heating at 160°C.

Conclusions

The thermal stability of PET may be successfully improved by the incorporation of highly aromatic sequences into its structure. This can be done by partially substituting DMT by DMN in the initial monomer mixture before polycondensation.

Copolymers containing 10, 20 and 80 wt.% of DMN and the fibres obtained from them have higher thermal stability than PET despite their smaller thermal resistance. Increasing the content of DMN in DMT/DMN copolymers causes a decrease in their flammability. The oxygen index (OI) values rise from 21.9% for PET to 26.9% for DMT/DMN 20/80 copolymer. The fibres obtained from the selected copolyesters demonstrate much better thermal stability than PET fibres alone. The improvement of the mechanical properties of copolyester fibres needs further efforts to optimise the conditions of their spinning and drawing.

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