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Thermal properties of wholly aromatic copolyamides and their blends

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Abstract

To modify some properties of poly(*p*-phenyleneterephthalamide) (PPTA), *m*-phenylene and 2,5-dichloroterephthaloyl groups were respectively introduced into its main chain by low-temperature solution copolycondensation and blending. Thermal properties of the two series of polymers obtained were studied using differential thermal analysis (DTA) and thermogravimetric analysis (TGA).

INTRODUCTION

Wholly aromatic polyamides are commercially important mainly as high-temperature fibers, e.g. Kevlar and Nomex. Although these polymers possess many desirable characteristics such as excellent mechanical properties and thermal stability, they are difficult to process because of their limited solubility and high glass transition or melt temperature [1–3]. Therefore, research has been directed to the synthesis of the more tractable high-temperature polymers which are melt-processable and/or soluble in organic solvents. One approach to increasing solubility and lowering glass transition temperature is the replacement of a hydrogen atom of the benzene ring by substituents such as alkyl, nitro or halogen groups; this leads to an increase in the solubility and fire resistance of the polymers [4–7]. Another approach is the introduction of a flexible group, such as *m*-phenylene or alkyl, into the main chain of wholly aromatic polyamides; it has been reported that these modified polymers have good solubility in available organic solvents and also flexibility [8].

Although many studies have been made of the synthesis and thermal characterization of *m*-phenylene in the main chain and chloro-substituents on the aromatic backbone, most have focused on copolycondensation which leads to an increase in the solubility, accompanied by an apparent decrease in the thermal stability of the polymers, but rarely on blending. In the present study, varying amounts of *m*-phenylene and 2,5-dichloroterephthaloyl were respectively introduced into the main chain of

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poly(*p*-phenyleneterephthalamide) (PPTA) by low-temperature solution copolycondensation and coblending. The thermal properties of the two series of polymers obtained by the two methods were investigated by differential thermal analysis (DTA) and thermogravimetric analysis (TGA).

EXPERIMENTAL

Preparation of copolyamides and their blends

Poly(*p*-phenyleneterephthalamide) (PPTA), poly(*m*-phenyleneisophthalamide) (Nomex), poly(*p*-phenylene-2,5-dichloroterephthalamide) (Cl-PPTA) with intrinsic viscosities of 5.21, 0.54, 0.54, respectively, and copolyamides were synthesized by low-temperature solution poly/copolycondensation in NMP-$CaCl_2$ (4–6%) according to literature methods [1–5]. Blends were prepared by solution coblending [9] in H_2SO_4.

Thermal analysis

A Shimadzu DT-40 thermal analyzer (DTA and TGA) was used to characterize the thermal properties of these copolyamides and blends. The rate of temperature increase in the non-isothermal run was 10°C min^{-1}, with nitrogen flowing at 50 cm^3 min^{-1}.

RESULTS AND DISCUSSION

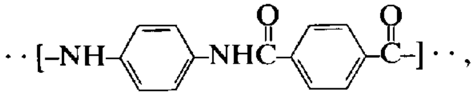
Scheme 1 shows the structures of the polymers obtained. Figure 1 shows typical DTA and TGA curves of the polymers. The thermal properties are summarized in Tables 1 and 2.

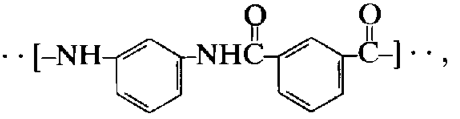
m-series containing *m*-phenylene:

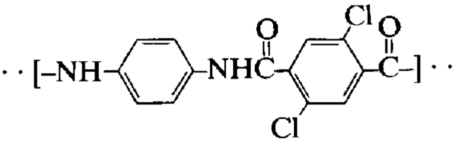
Random copolymer: ··[···AABABBA···]··; blend: ··[·A·]·· mixed with ··[·B·]··

Cl-series containing 2,5-dichloroterephthaloyl:

Random copolymer: ··[···AACACCA···]··; blend: ··[·A·]·· mixed with ··[·C·]··

A is 

B is 

C is 

Scheme 1.

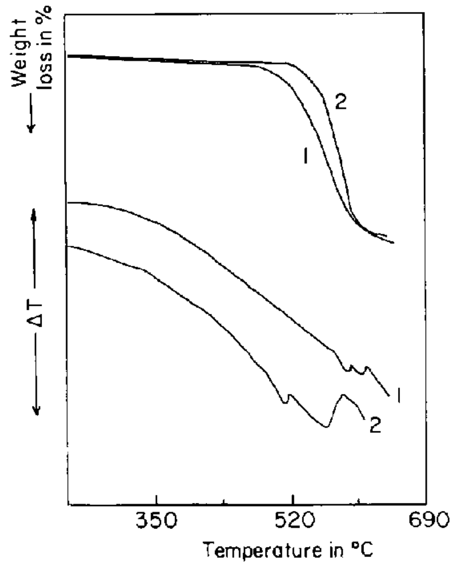


Fig. 1. Typical DTA and TGA curves of copolyamide containing 10% 2,5-dichloroterephthaloyl group (curve 1) and of PPTA (curve 2).

The experimental results were compared to those of the parent polymer PPTA which has a decomposition temperature T_d and 10% weight-loss temperature $T_{10\%}$ in N_2 of 542°C and 568°C, respectively. Thus, for both the *m*-series containing *m*-phenylene and the Cl-series containing 2,5-dichloroterephthaloyl, both the T_d and $T_{10\%}$ of the copolymers and blends apparently decrease with increasing levels of the third ingredient, i.e. the modified polymers were much less thermally stable, but the T_d and $T_{10\%}$ values of all the polymers remained above 410°C and 465°C, respectively.

In the *m*-series, the thermal stability of the blends was clearly better than that of the corresponding copolymers, e.g. the T_d of the blend containing 30% *m*-phenylene was 521°C, cf. 440°C for the copolymer. In the Cl-series, however, the thermal stability of the blends was worse than those of the copolymers with the same amount of 2,5-dichloroterephthaloyl. The results above demonstrated that in order to avoid substantially decreasing the thermal stability of a modified polymer, *m*-phenylene is best introduced into the main chain of PPTA by blending, whereas copolycondensation is preferable for introducing 2,5-dichlorotetrephthaloyl. This is shown in the excellent mechanical and thermal properties and fire resistance (LOI 34) of a fiber successfully synthesized by random copolycondensation of 2,5-dichloroterephthaloyl as third monomer [5].

However, introducing the same amount of the third ingredient in the two series, the decrease in thermal stability of the polymer on introducing *m*-phenylene was much less than that on introducing 2,5-dichlorotetrephthaloyl. The introduction of two chlorine atoms in the ortho

TABLE 1

Thermal properties in nitrogen of polyamides containing *m*-phenylene

Composition of chain segment of polymer/mol%		Copolymers			Blends		
		T_d/°C [a]	$T_{10\%}$/°C [b]	T_p/°C [c]	T_d/°C [a]	$T_{10\%}$/°C [b]	T_p/°C [c]
A	B						
100	0	542.5	568.6	560.4	542.5	568.6	560.4 PPTA
90	10	489.3	549.9	522.3	530.9	557.3	513.7
85	15	449.3	527.3	536.0	527.5	562.3	– [d]
70	30	440.2	494.2	544.6	521.1	551.4	519.4
				570.3			584.8
50	50	411.6	481.8	291.4	489.9	535.3	– [d]
				547.6			
				602.0			
30	70	410.7	480.8	316.7	431.1	465.3	444.0
				478.2			499.9
				555.5			572.1
0	100	411.1	474.1	312.3	411.1	474.1	312.3
(Nomex)				476.9			476.9
				581.2			581.2

[a] Temperature of initial decomposition. [b] Temperature of 10% weight loss. [c] All the DTA peaks were endothermic. [d] No observation of exo/endotherm.

TABLE 2

Thermal properties of polyamides containing 2,5-dichloroterephthaloyl

Composition of chain segment of polymer/mol%		Copolymers			Blends		
		T_d/°C	$T_{10\%}$/°C	T_p/°C	T_d/°C	$T_{10\%}$/°C	T_p/°C
A	C						
100	0	542.5	568.6	560.4	542.4	568.6	560.4 PPTA
				584.5			584.5
90	10	491.2	550.4	566.6	485.3	531.6	559.0
				592.3			580.2
85	15	475.3	536.8	–	459.2	528.4	517.7
70	30	461.2	517.9	532.1	460.7	518.3	552.1
							568.3
50	50	461.3	504.2	533.4	455.0	496.1	563.7
30	70	445.2	490.1	–	453.3	488.8	–
0	100	446.7	487.9	496.2	446.7	487.9	496.2
(Cl-PPTA)							

Key: see Table 1.

position to the carbonyl could lead to strong intramolecular hydrogen bonding between the chlorine atom and the hydrogen atom of the amide group. The strong hydrogen binding in turn might induce chain scission at a high temperature, which could account for the higher decrease in thermal stability.

After modification of the polymers, their thermal transition temperatures T_p (see Tables 1 and 2) were higher than that of Nomex or Cl-PPTa, but lower than that of PPTA. When the amount of *m*-phenylene or 2,5-dichlorophthaloyl introduced was less than 30%, the DTA curves of the modified polymers displayed two endothermic peaks, similar to that of PPTA. When more than 50% was added, the DTA curves were similar to those of Nomex or Cl-PPTA. This result shows that the three chain segments, A, B, or C, contribute to the thermal properties of the polymers to an extent proportional to the amount of each present.

Owing to the presence of the polar amide linkage and the polar Cl substituent, the polyamides absorb significant amounts of moisture and the TGA curves show a small weight loss in the range 45–125°C, due to water desorption. We believe that the amount of water absorbed (either chemical or physical absorption) and the temperature of its loss, together with the thermal properties of the polymer, are closely associated with its molecular symmetry, the degree of order of the molecular chain and the synthesis mode.

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