# Novel regular network wholly aromatic polyester and polyamide films

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Novel regular network wholly aromatic polyester and polyamide films were prepared from trimesic acid (Y) and aromatic diols and aromatic diamines. Prepolymers prepared by melt polycondensation were cast from dimethylformamide solution and post-polymerized at various elevated temperatures and times to form networks. The resultant films were insoluble in any organic solvents. Heat distortion temperature $T_h$ of both polyester and polyamide films increased with increasing post-polymerization temperature and time. Polyester films of OY, prepared from Y and 4,4'-dihydroxybiphenyl ether (O) post-polymerized at 290°C for 18 h, and of BY, prepared from Y and 4,4'-dihydroxybiphenyl (B) post-polymerized at 340°C for 2 h, showed the highest $T_h$ (430°C) of the polyester films studied. Polyamide films of O'Y, prepared from Y and 4,4'-diaminobiphenyl ether (O') post-polymerized at 350°C for 2 h, had the highest $T_h$ (444°C) of the polyamide films studied. The degree of reaction, a measure of network formation, increased with increasing post-polymerization time. X-ray diffraction patterns of these network polymer films exhibited broad but distinct diffraction peaks, suggesting the formation of some ordered structure owing to the regular network formed by symmetrical trimesic acid moiety. The density of polyester films decreased and that of polyamide films increased with increasing post-polymerization time. These network polymers had tensile strengths and Young's moduli lower than the network polyester film of 2GY prepared from Y and ethylene glycol (2G). Temperature profiles of both thermomechanical analysis and thermogravimetry of polyamide films exhibited higher thermal resistance than polyester films, suggesting the formation of a carbonized structure at higher temperature.

(**Keywords: wholly aromatic polyesters and polyamides; regular network polymer films; high thermal distortion temperature**)

## INTRODUCTION

In recent years, various super-engineering plastics have been developed, such as poly(phenylene sulphide)s, poly(ether sulphone)s, poly(ether ketone)s, polyimides and polyarylates, which have superior thermal stability and excellent mechanical properties. Aramid has also been a commercially important fibre, having higher strength and higher modulus. The main reason for the high performances of super-engineering plastics is the rigid structure due to the aromatic rings.

We have already reported the novel regular network aromatic–aliphatic polyester films[1–3] from multifunctional aromatic carboxylic acids and glycols, and aromatic–aliphatic polyamide films[4] from trimesic acid and aliphatic diamines, and have shown that they have a high resistance to thermal distortion and some ordered structure. Furthermore, network aromatic–aliphatic polyamide fibre produced by reaction spinning followed by post-polymerization has also been investigated[5].

More recently, we have prepared wholly aromatic network polyester films from trimesic acid and aromatic diols and corresponding polyamide films from trimesic acid and aromatic diamines, and found that they have much higher resistance to thermal distortion. In this paper, we report the preparation of these wholly aromatic network polyester and polyamide films, and discuss their thermal and mechanical properties in relation to their chemical structures.

## EXPERIMENTAL

### *Monomers*

Structural formulas and codes of the monomers used in this study are shown in *Figures 1* and *2* for polyesters and polyamides, respectively. Triphenyl ester of trimesic acid (Y) was obtained by refluxing trimesoyl trichloride with phenol at 175–200°C for 1 h, and recrystallized from a mixed solvent of toluene and methanol. The obtained triphenyl ester of Y had a melting point of 172–173°C. Aromatic diols and diamines were used as received.

### *Preparation of prepolymers*

*Polyester prepolymer.* A mixture of 0.004 mol triphenyl ester of Y and 0.006 mol aromatic diol was heated in a stream of nitrogen with zinc acetate as a catalyst under the conditions shown in *Table 1.*

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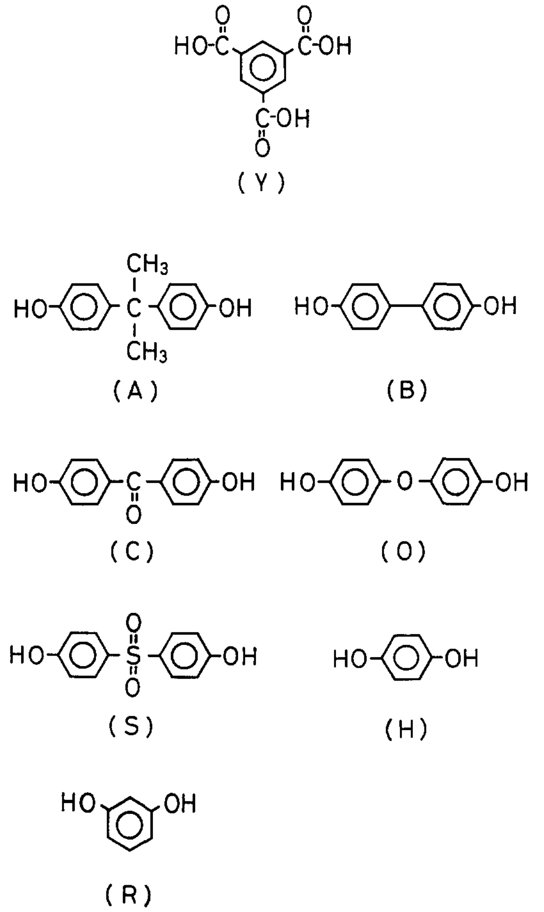

**Figure 1** Structural formulas and codes of monomers for polyesters

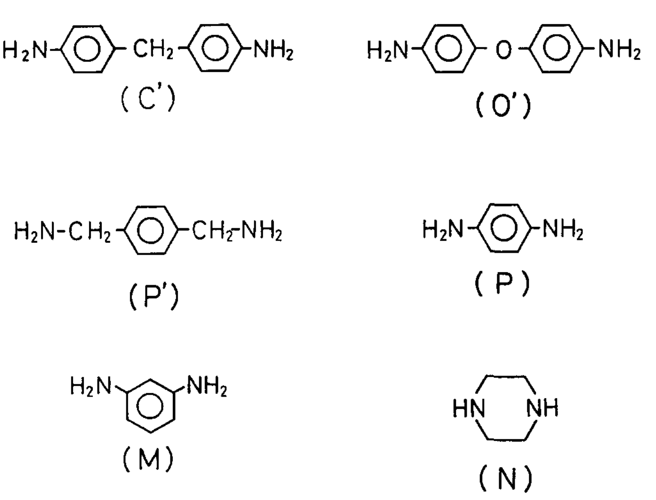

**Figure 2** Structural formulas and codes of monomers for polyamides

**Table 1** Preparation conditions of polyester prepolymers

| Prepolymer | Preparation condition |
|---|---|
| AY | 240°C, 1 h → 260°C, 30 min |
| BY | 240°C, 2 h → 265°C, 30 min |
| CY | 240°C, 1 h → 280°C, 100 min → 280°C, 20 min *in vacuo* |
| HY | 240°C, 1 h → 260°C, 45 min |
| OY | 240°C, 1 h → 260°C, 30 min |
| RY | 240°C, 1 h → 260°C, 60 min → 280°C |
| SY | 240°C, 1 h → 260°C, 60 min → 290°C, 20 min → 300°C, 15 min *in vacuo* |

**Table 2** Preparation conditions of polyamide prepolymers

| Prepolymer | Preparation condition |
|---|---|
| C′Y | 180°C, 1 h → 200°C, 25 min |
| MY | 180°C, 1 h → 200°C, 1 h → 215°C |
| NY | 180°C, 5 min |
| O′Y | 200°C, 43 min |
| PY | 200°C, 45 min |
| S′Y | 240°C, 1 h → 260°C, 1 h → 280–290°C *in vacuo* |

*Polyamide prepolymer.* A mixture of 0.004 mol triphenyl ester of Y and 0.006 mol aromatic diamine was heated in a stream of nitrogen under the conditions shown in *Table 2.*

### *Preparation and post-polymerization of films*

The obtained prepolymer was cast on an aluminium plate from 11 wt% dimethylformamide solution at ~60–130°C. The cast film was heated to a given temperature at a heating rate of 5°C $\mathrm{min}^{-1}$ and held at this temperature for a given time in a stream of nitrogen for post-polymerization. The aluminium substrate was then dissolved off in a 10% hydrochloric acid and a 10% sodium hydroxide aqueous solution for polyester and polyamide films, respectively. Transparent and flexible films were obtained which were insoluble in organic solvents.

### *Characterization*

Thermomechanical analysis (t.m.a.) was performed in penetration mode under a pressure of 10 kg $\mathrm{cm}^{-2}$ and a heating rate of 10°C $\mathrm{min}^{-1}$ in nitrogen atmosphere, using a Shimadzu model DT-30 thermomechanical analyser.

Density was measured in a heptane–carbon tetrachloride density gradient column at 30°C within ±0.1°C accuracy.

The X-ray diffraction intensity curve was measured with a Toshiba model ADG-301 X-ray diffractometer with nickel filtered CuKα radiation.

Tensile properties were measured with a Shimadzu model IM-100 autograph at an extension rate of 100% $\mathrm{min}^{-1}$.

Thermogravimetry (t.g.) was performed on a Shimadzu model DT-30 thermogravimetric analyser at a heating rate of 10°C $\mathrm{min}^{-1}$ in nitrogen atmosphere.

### *Estimation of degree of reaction*

The degree of reaction was determined by measuring the concentration of unreacted phenyl ester group in the prepared network polyester films. The total concentration of unreacted phenyl ester group in the monomer unit was determined as follows. A sample of polyester film (0.5 g) was alkali-hydrolysed in 40 g of 15% sodium hydroxide aqueous solution at 90°C for 48 h. After cooling, the solution was neutralized with hydrochloric acid and filtered to remove the precipitated monomers. Phenol was extracted with 500 ml of ethyl ether from filtrate and the extracted ethyl ether solution was concentrated. The amount of phenol extracted was determined by a Shimadzu model GC-4C gas chromatograph with PEG-6000 column, using *o*-dichlorobenzene as an internal standard.

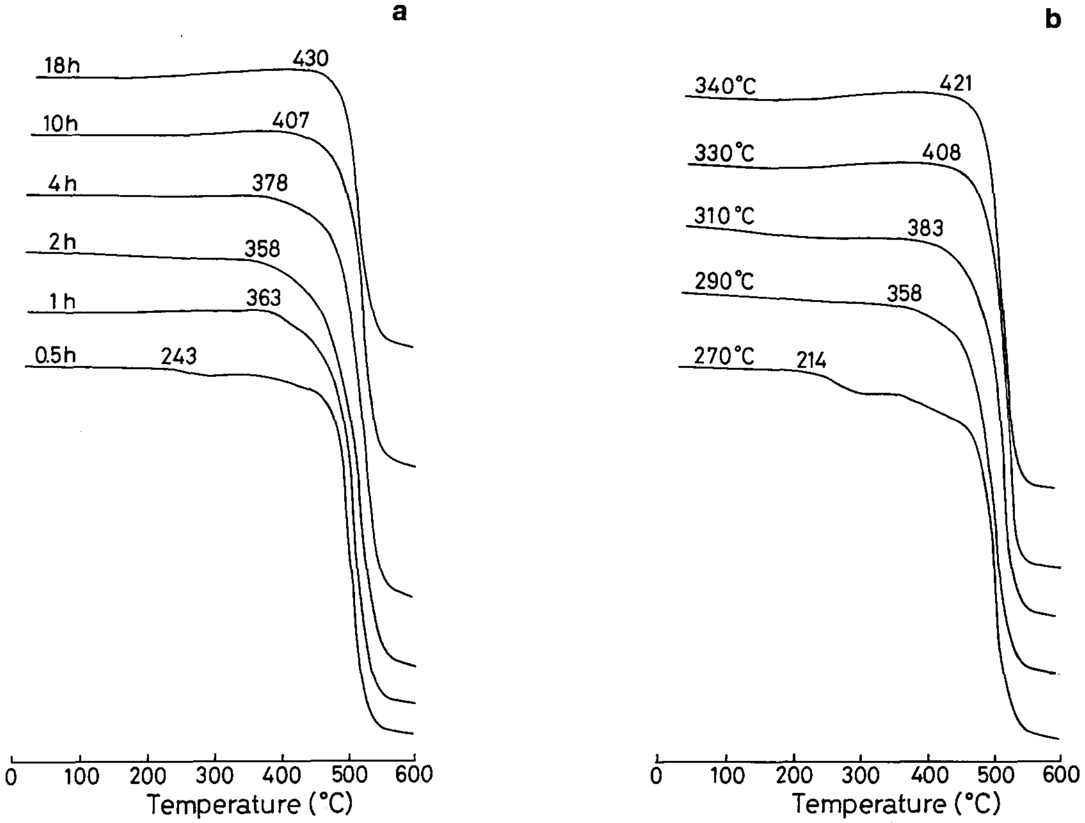

**Figure 3** T.m.a. temperature profiles of OY polyester films: (a) post-polymerized for various times at a constant temperature of 290°C; (b) post-polymerized at various elevated temperatures for a constant time of 2 h

## RESULTS AND DISCUSSION

### *Condition of post-polymerization*

*Figure 3* shows t.m.a. temperature profiles of OY polyester films when post-polymerized for various times at a constant temperature of 290°C (*Figure 3a*) and post-polymerized at various elevated temperatures for a constant time of 2 h (*Figure 3b*). The corresponding t.m.a. temperature profiles of O'Y polyamide films are shown in *Figure 4*. Two-step penetration behaviour is observed for both OY and O'Y films subjected to post-polymerization for a shorter time and at a lower temperature, whereas for a longer time and a higher temperature of post-polymerization, heat distortion is not observed until the final penetration by thermal decomposition. The same behaviour was also observed for the network polyester films prepared from aromatic tetracarboxylic acids and ethylene glycol[1,3]. The heat distortion temperature $T_h$ is defined by the first inflection point in the t.m.a. temperature profile, shown in *Figures 3* and *4*. Similar t.m.a. temperature profiles were obtained for the other polyester and polyamide films studied.

The effect of the post-polymerization time and temperature on $T_h$ are shown in *Figure 5* for polyester films and in *Figure 6* for polyamide films. The $T_h$ values of polyester and polyamide films increase with increasing post-polymerization time and then level out; they also increase with increasing post-polymerization temperature, implying that the mobility of molecular chains is more suppressed by the network formation. Post-polymerization above 350°C gave rise to thermal decomposition of films.

OY and BY showed the highest $T_h$ (430°C) of the polyester films studied, and O'Y had the highest $T_h$ (444°C) of the polyamide films studied.

### *Degree of reaction*

The degree of reaction for post-polymerization at 290°C was measured for AY, BY and OY polyester films. Degree of reaction increased with increasing post-polymerization time: AY film had degrees of reaction of 82%, 83% and 88% for post-polymerization times of 0.5, 4 and 18 h, respectively; OY film had degrees of reaction of 87%, 90% and 96% for corresponding post-polymerization times. The degree of reaction of BY polyester film was 94% for 18 h. These values of the network wholly aromatic polyester films are almost comparable to those of the network aromatic–aliphatic polyester films reported before[3].

### *Structure and properties of post-polymerized films*

*Figure 7* shows X-ray diffraction intensity curves of various network polyester and polyamide films post-polymerized at 290°C for 18 h. AY has two distinct peaks, but the others have broader peaks. Similar but more distinct peaks in the X-ray intensity curves have previously been obtained for the network aromatic–aliphatic polyester films[1–3] and polyamide films[4], which suggests some ordered structure owing to the regular network by symmetric trimesic acid moiety. The formation of some ordered structure is also assumed for these wholly aromatic network polymers, but the degree of ordering is lower than for previously reported network

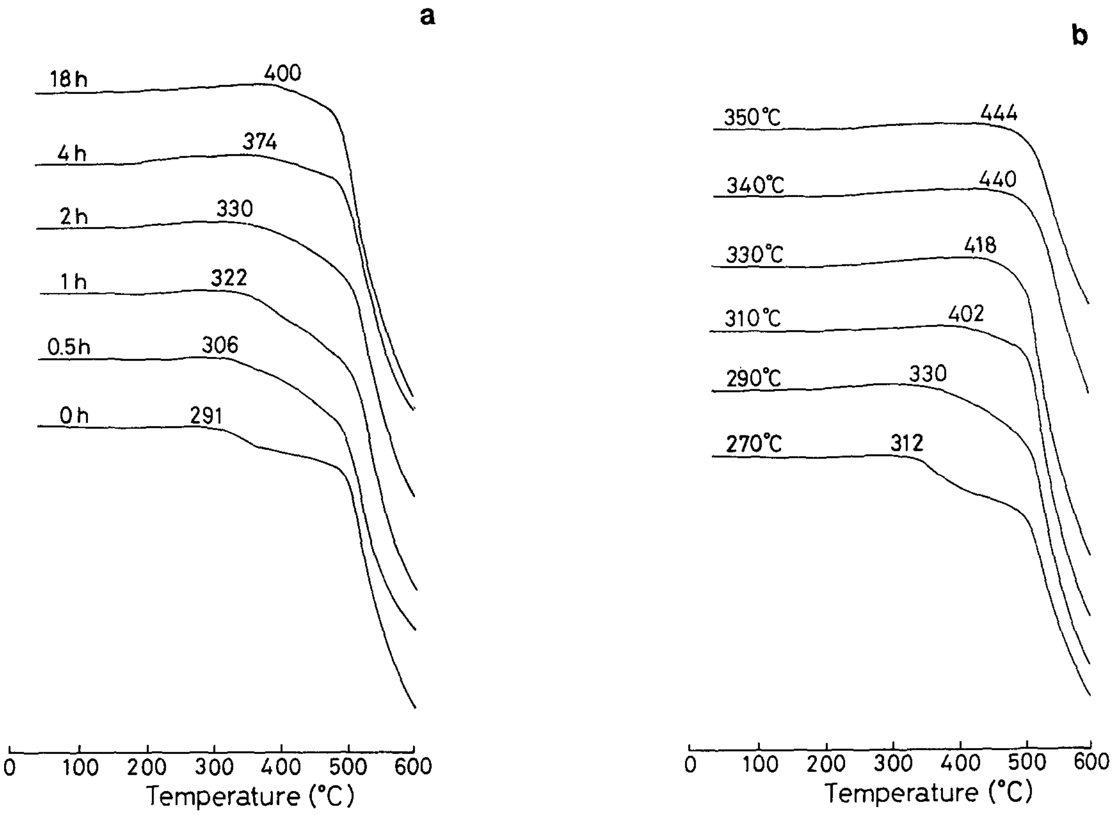

**Figure 4** T.m.a. temperature profiles of O'Y polyamide films: (a) post-polymerized for various times at a constant temperature of 290°C; (b) post-polymerized at various elevated temperatures for a constant time of 2 h

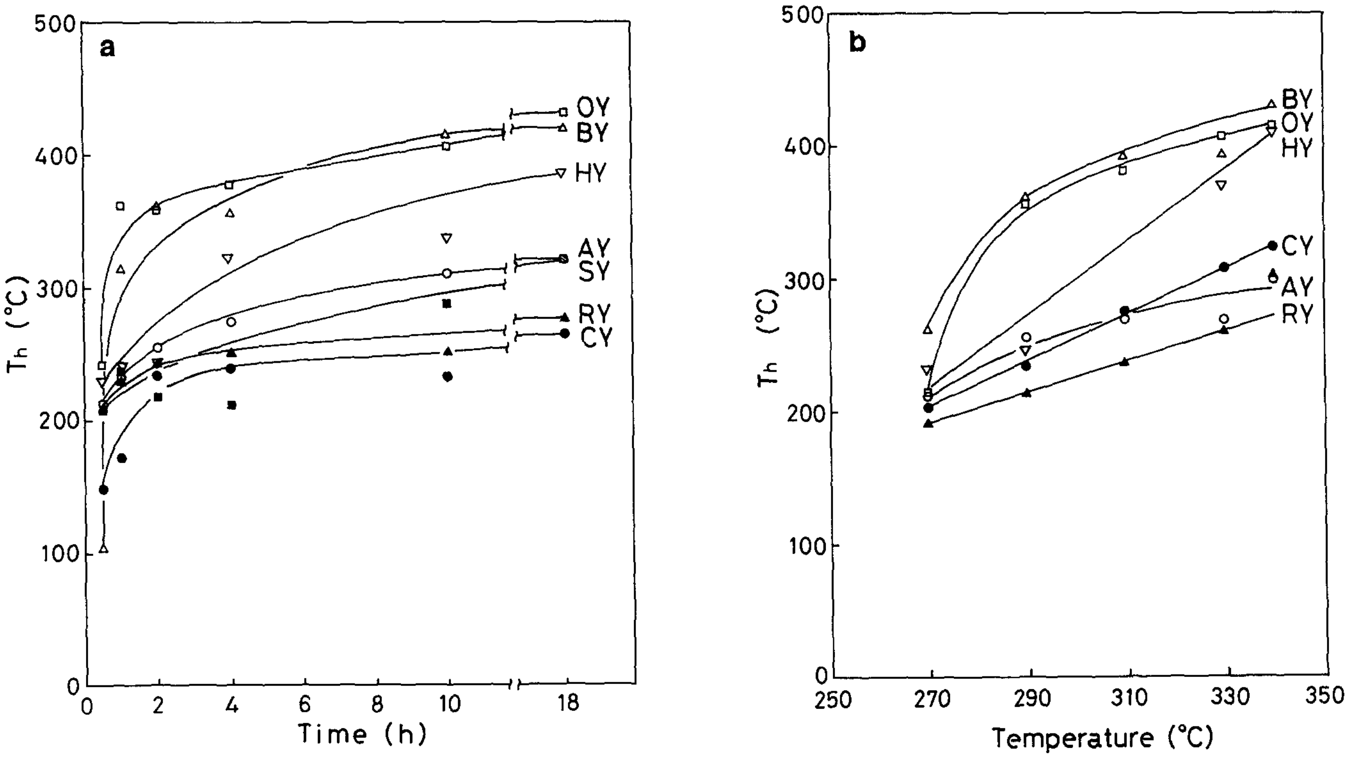

**Figure 5** Effect of (a) post-polymerization time (at constant temperature of 290°C) and (b) post-polymerization temperature (at constant time of 2 h) on $T_h$ for polyester films

polymers having aliphatic chains, since there is less flexibility due to the rigid structure.

Densities of various network polyester and polyamide films are plotted against the post-polymerization time in *Figure 8*. The post-polymerization temperature was 290°C. Densities of the polyester films post-polymerized for 0.5 and 1 h could not be measured because these films were swelled in the density gradient medium. It is interesting that the density of polyester films decreases with increasing post-polymerization time, while the

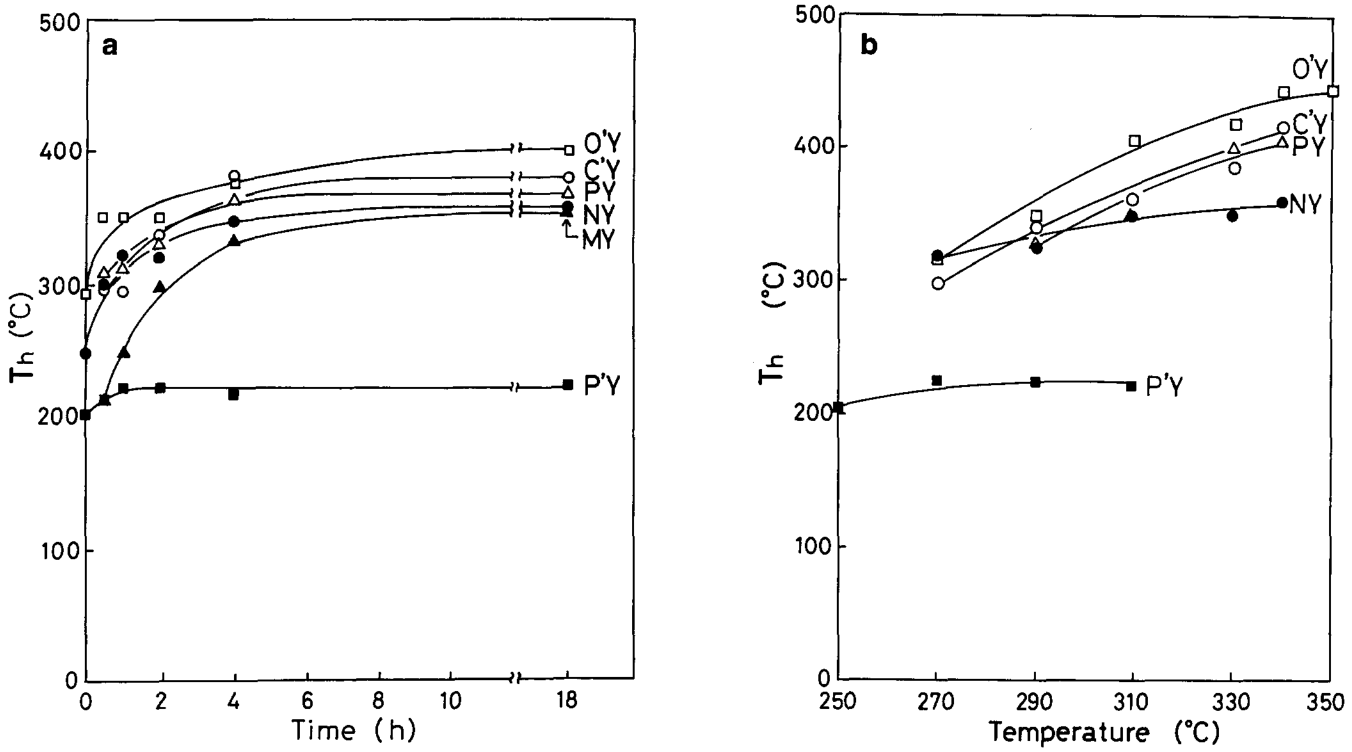

**Figure 6** Effect of (a) post-polymerization time (at constant temperature of 290°C) and (b) post-polymerization temperature (at constant time of 2 h) on $T_h$ for polyamide films

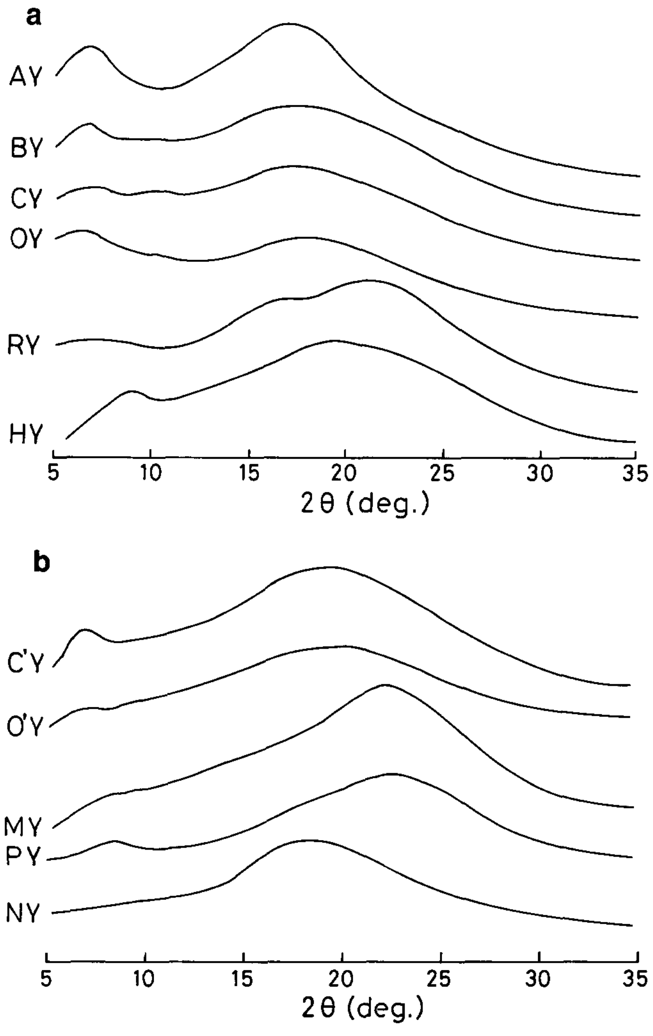

**Figure 7** X-ray diffraction intensity curves of (a) polyester and (b) polyamide films, post-polymerized at 290°C for 18 h

**Table 3** Mechanical properties of polyester and polyamide films post-polymerized at 290°C for 4 h in comparison with those of 2GY previously reported[1,2]

| Polymer | Tensile strength (kg mm$^{-2}$) | Young's modulus (kg mm$^{-2}$) | Elongation (%) |
|---|---|---|---|
| AY | 5.4–6.6 | 166–193 | 4.0–5.2 |
| BY | 5.8–6.9 | 161–178 | 6.1–8.7 |
| CY | 6.2–7.8 | 161–187 | 3.4–4.2 |
| OY | 5.7–6.2 | 163–172 | 4.8–6.8 |
| HY | 4.5–5.9 | 132–169 | 5.3–7.2 |
| 2GY[a] | 8.4 | 223 | 8.0 |
| C'Y | 5.0–8.2 | 182–210 | 4.8–6.3 |
| O'Y | 5.2–7.5 | 232–263 | 3.2–6.4 |

[a] Post-polymerized at 260°C for 4 h

density of polyamide films increases; similar behaviour has been observed for network aromatic–aliphatic polyester films[1–3] and polyamide films[4], respectively. The lowest density of AY may be responsible for the larger free volume due to the bulky isopropylidene group. The highest density of SY is caused by the presence of the sulphone group.

*Table 3* summarizes the mechanical properties of AY, BY, CY, OY and HY polyester films and C'Y and O'Y polyamide films post-polymerized at 290°C for 18 h; the mechanical properties of 2GY polyester film from trimesic acid and ethylene glycol[1,2] are given for comparison. It is noted that values of Young's modulus for wholly aromatic polyester films are lower than for aromatic–aliphatic 2GY film irrespective of the higher content of the rigid benzene ring. This may be ascribed to the longer diol units and consequent lower crosslinking densities of these wholly aromatic network polyester

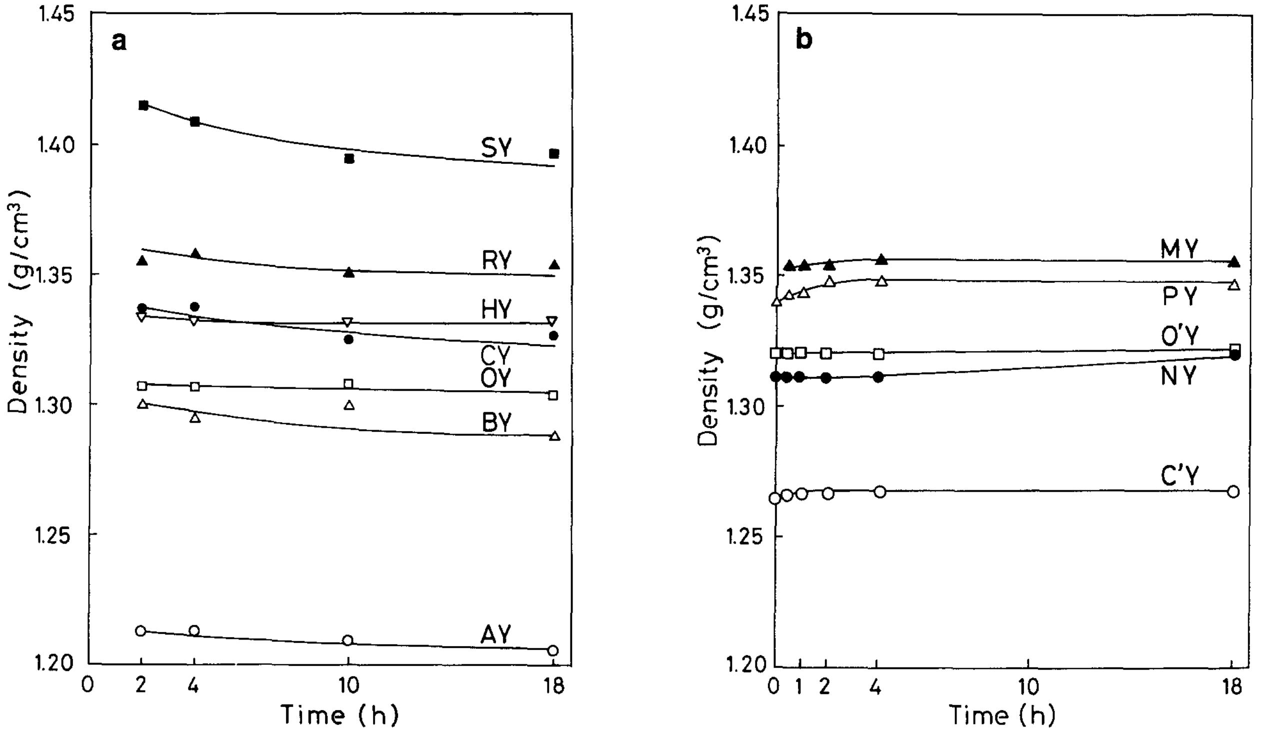

**Figure 8** Effect of post-polymerization time on densities of (a) polyester and (b) polyamide films. Post-polymerization temperature is 290°C

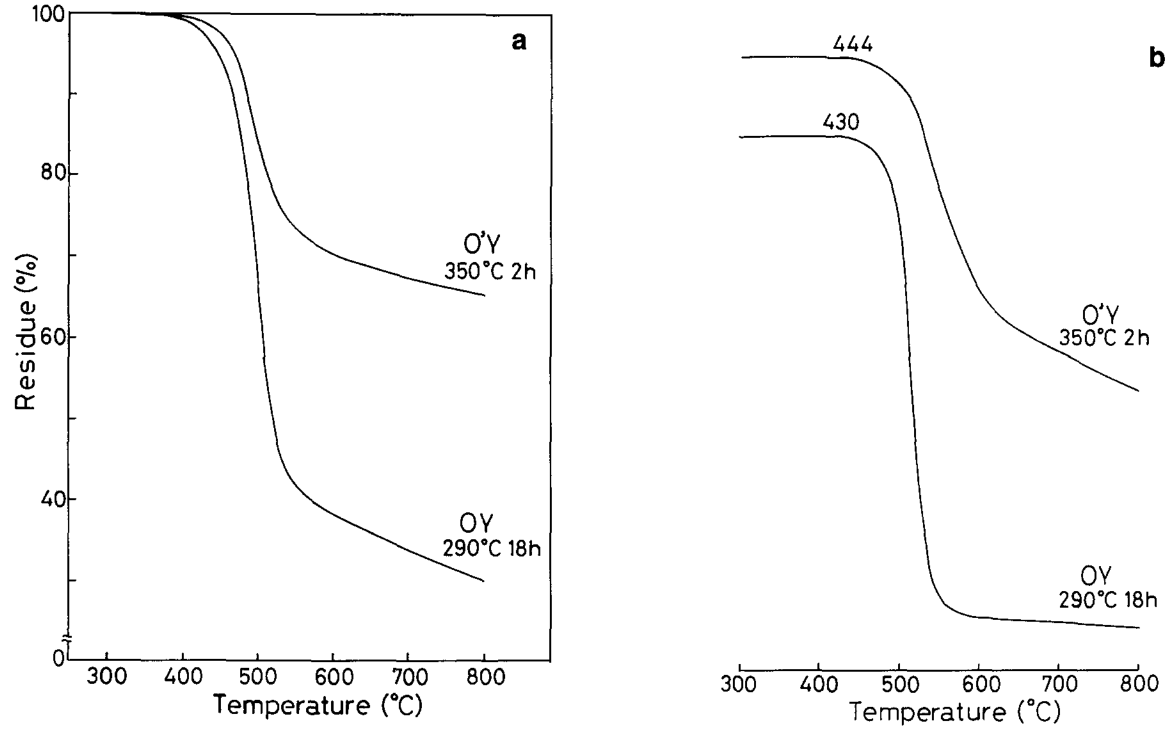

**Figure 9** (a) T.g. and (b) t.m.a. temperature profiles of OY polyester and O'Y polyamide films post-polymerized at 290°C for 18 h and at 350°C for 2 h, respectively

films; this corresponds to the lower densities of these polyester films compared to that of 2GY[1,2], $1.395\ \mathrm{g\,cm^{-2}}$.

*Figures 9a* and *b* show, respectively, the t.g. and t.m.a. temperature profiles of OY polyester and O'Y polyamide films having the same diphenyl ether group. The t.m.a. temperature profile is quite similar to the t.g. temperature profile, suggesting that the final penetration occurs by thermal decomposition. The initial decomposition temperature of O'Y is 390°C, which is 20°C higher than that of OY, corresponding well to the difference in $T_h$ value between them. The residue of O'Y at 800°C is much greater than that of OY, suggesting the formation of a carbonized structure of O'Y polyamide at higher temperature. The formation of a carbonized structure of O'Y provides the higher thermal resistance not to penetrate a probe completely at 800°C as shown in *Figure 9b*. Similar differences were observed on the t.g. and t.m.a. temperature profiles for the other wholly aromatic polyester and polyamide films.

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