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# Surface modification of aramid fibres

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The surface of poly-*p*-phenylene terephthalamide fibres was chemically modified using oxalylchloride to obtain an intermediate on which various secondary reactions were performed. The adhesion to epoxy resins, as measured by multifilament pull-out tests, was markedly improved (by up to 70%) by this treatment and fibre properties were not affected.

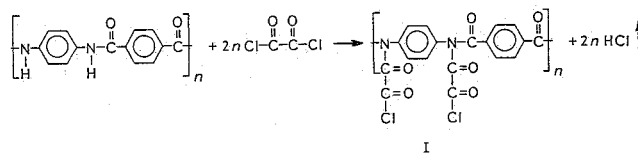
(Keywords: aramid fibre; surface modification; oxalylchloride; adhesion; epoxy resin)

## Introduction

Poly(*p*-phenylene terephthalamide) (PPTA) fibres, well known under the tradenames Kevlar (Du Pont) and Twaron (Akzo), possess excellent mechanical properties and a good thermal stability<sup>1,2</sup>. These excellent mechanical properties, in combination with a low density ( $\rho = 1.45 \text{ g/cm}^3$ ) make these fibres particularly suitable for the use as a reinforcement in high performance-low weight composite materials. However, whether the properties of the fibre can effectively be imparted to the composite depends on the adhesion between reinforcement and matrix. The adhesion between PPTA fibres and most matrices is poor, due to their chemical inertness and smooth surface which prevent chemical as well as mechanical bonding. To overcome this problem several methods have been developed. Among these are surface roughening of the fibres<sup>3,4</sup>, the use of coatings<sup>5,6</sup> and the introduction of functional groups by either physical<sup>7,8</sup> or chemical<sup>9,10</sup> methods. An obvious requirement of any surface treatment procedure is that it should not affect the mechanical properties of the reinforcement or at least not to a large extent (less than 10%). In this communication we report on a chemical method for the surface modification of PPTA fibres resulting in an increased adhesion with epoxy resins without deterioration of the mechanical properties of the fibres themselves<sup>11</sup>.

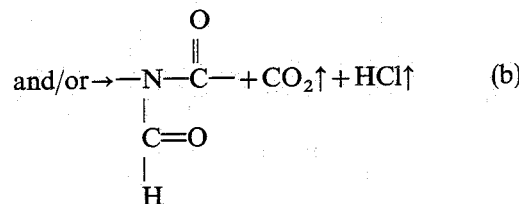
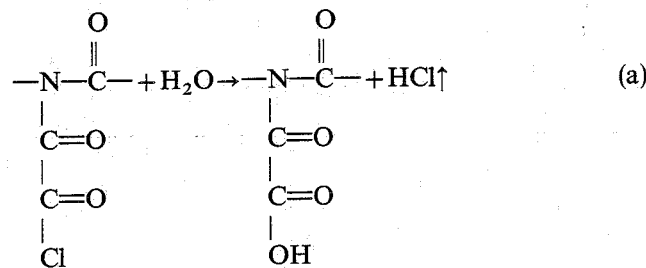
## Experimental

**Reactions.** The sizing of the PPTA fibres used throughout this study (Twaron D1000) was removed by Soxhlet extraction in dichloromethane, prior to all experiments. The surface treatment procedure comprised two successive stages. At first the PPTA fibres, loosely wound around a glass cage-like support, were immersed in a hot (50–60°C) solution of sulpholane/oxalylchloride (9:1 vol/vol) for 1 h. In later studies<sup>12</sup> it will be shown that much shorter times can be used in actual practice. According to reference 13 and model compound studies<sup>14</sup> *N*-acylation takes place.

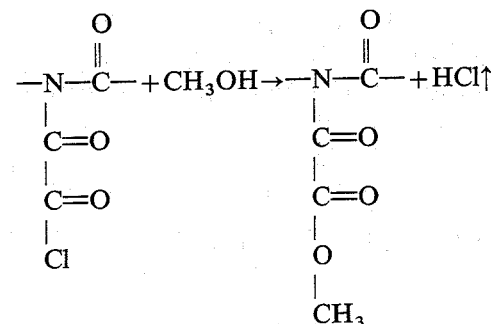


Scheme 1

The formation of intermediate I is the key step in the process in that it provides a highly reactive intermediate. In a subsequent reaction step the I-surface modified fibres are substituted with different functional groups by reaction with water (Scheme 2), methanol (Scheme 3), ethylenediamine (Scheme 4) or glycidol (Scheme 5).



Scheme 2 Water

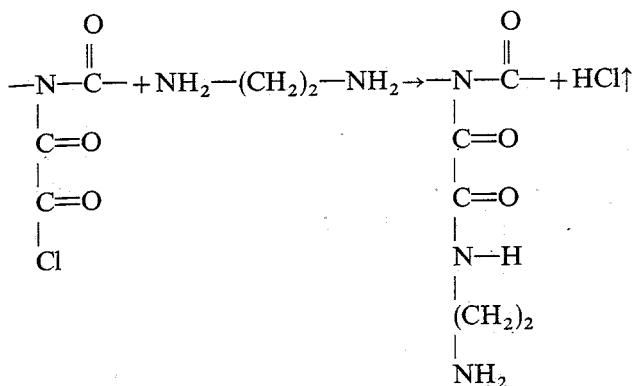


Scheme 3 Methanol

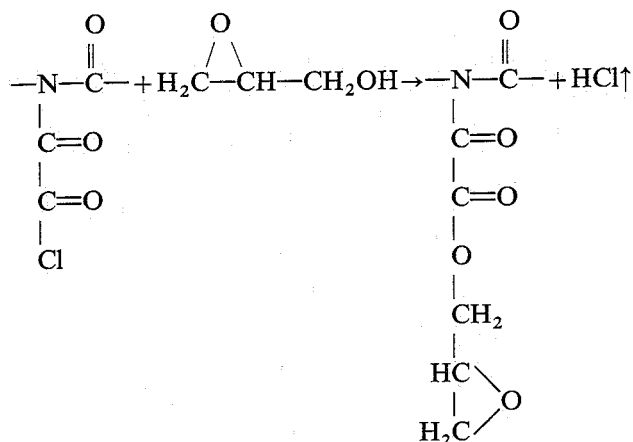
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Scheme 4 Ethylenediamine



Scheme 5 Glycidol

For the modifications outlined in Schemes 2 and 3 the I-modified fibres were simply immersed in the reagent solutions, distilled water or methanol, followed by rinsing with distilled water or methanol. A slightly different procedure was used in the other cases. Before the I-modified fibres were immersed in ethylenediamine, the fibres were rinsed with dry dichloromethane to remove excess oxalylchloride adhering to the fibre surface which otherwise would give rise to (homo)polymer formation. For the same reason rinsing with dry diethyl ether was performed prior to the immersion of the I-modified fibres in a glycidol/diethyl ether solution. Excess glycidol was removed by subsequent rinsing with diethyl ether. All the surface modified fibres were dried *in vacuo* and stored in a desiccator.

The introduced amine, epoxy or aldehyde/acid groups may or may not participate in subsequent covalent bonding with a curing epoxy resin network. These groups and the ester groups are capable of forming hydrogen bonds with the hydroxyl groups of the resin network. The effect of the surface treatment, described above, on fibre-matrix bonding was measured using a multifilament pull-out test<sup>15</sup>. Specimen preparation consisted of taking two strands of PPTA fibres, which were subsequently twisted by 1 turn/cm and embedded in a disk of epoxy resin (1.5–2 mm thick). Testing was performed at a speed of 1 mm/min. To compare the different results, the maximum force measured during pull-out was divided by the embedded length of the fibre bundle. Furthermore, the bundle pull-out shear strength (BPS) was calculated. BPS is defined as:

$$\text{BPS} = P/\pi dl$$

where  $P$  = maximum force measured during pull-out (N);  $d$  = diameter of the fibre bundle (mm); and  $l$  = embedded length of fibre bundle (mm).

The PPTA fibres used for the determination of the mechanical properties were also twisted by 1 turn/cm. The strain rate was 10%/min and closed loop operation made accurate constant strain rate experiments possible. X-ray photoelectron spectroscopy (x.p.s.) spectra were recorded on a Physical Electronics 550 x.p.s./AES spectrometer. Operating conditions of the X-ray source were 10 kV and 40 mA. Pressure did not exceed  $5 \times 10^{-8}$  torr. A sweep time of 20 min per element was used for the detailed recordings. The sample was placed under an angle of 50° towards the analyser.

### Results and discussion

The surface composition of PPTA fibres and surface modified PPTA fibres, as measured with x.p.s. and expressed as the carbon to nitrogen to oxygen ratio, together with the calculated values according to the reaction schemes outlined above, are given in Table 1. Note that the PPTA fibres exhibit an oxidized surface in agreement with the findings of Penn and Larsson<sup>16</sup> and Allred<sup>8</sup>.

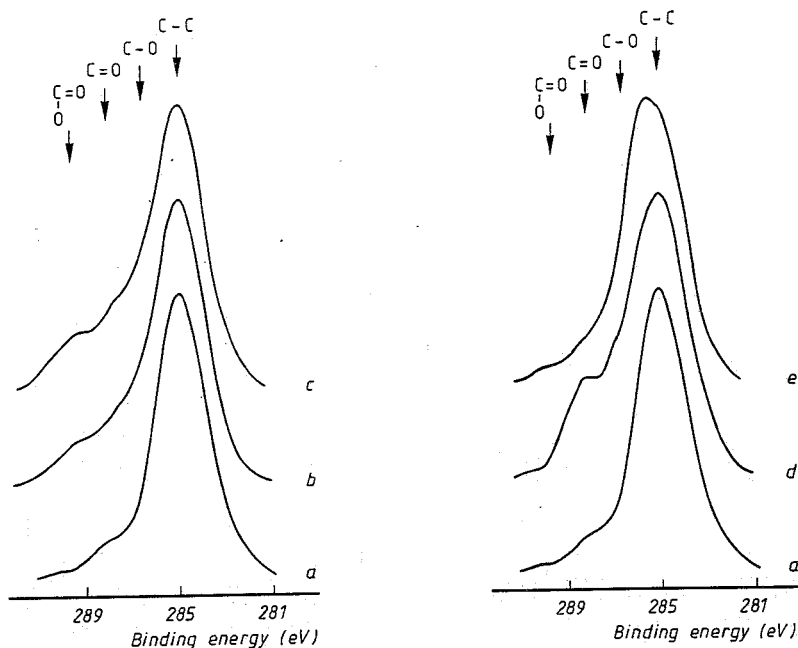
Information about the nature of the incorporated groups can be obtained from high resolution C<sub>1s</sub>, O<sub>1s</sub> and N<sub>1s</sub> spectra. The C<sub>1s</sub> spectra, shown in Figure 1, are the most informative. The binding energy of carbon in hydrocarbons is 285 eV. Introduction of oxygen, however, induces shifts to higher binding energies. No

Table 1 Effect of various treatments on surface composition of Twaron D1000 aramid fibres

Treatment	X.p.s. measured/calculated		
	%C	%N	%O
None	77/77.8	8/11.1	15/11.1
Oxalylchloride-water	70/64.3 <sup>a</sup> /72.7 <sup>b</sup>	5/7.1 <sup>a</sup> /19.1 <sup>b</sup>	25/28.6 <sup>a</sup> /18.2 <sup>b</sup>
Oxalylchloride-methanol	67/66.7	5/6.6	28/26.7
Oxalylchloride-ethylenediamine	65/64.7	17/17.6	18/17.6
Oxalylchloride-glycidol	70/66.7	6/5.6	24/27.7

<sup>a</sup> Calculated value according to reaction Scheme 2a

<sup>b</sup> Calculated value according to reaction Scheme 2b



**Figure 1** High resolution  $C_{1s}$  spectra of Twaron D1000 aramid fibres. Curve a, untreated; curve b, oxalylchloride-water treated; curve c, oxalylchloride-methanol treated; curve d, oxalylchloride-ethylenediamine treated; curve e, oxalylchloride-glycidol treated

significant shifts are observed upon introduction of nitrogen. These shifts relative to  $C_{1s}$  (hydrocarbon) are 1.5 eV for ether/epoxy, 3 eV for carbonyl and 4.5 eV for ester/acid groups<sup>17,18</sup>. Note that the observed differences between the  $C_{1s}$  spectra of surface modified PPTA fibres and native PPTA fibres, when viewed in terms of the introduction of the aforementioned carbon-oxygen groups, are consistent with the reaction schemes outlined above.

The effect of various surface treatments on mechanical properties of the PPTA fibres as well as on the adhesion to epoxy resin is shown in *Table 2*. The tensile strength of the PPTA fibres is not affected, suggesting that the procedure is limited to the outer surface layers. The maximum improvement in adhesion relative to virgin PPTA fibres is 70%. Similar results were reported by Elkink *et al.* for a modification procedure<sup>15</sup>. They also showed that due to this increase, shear failure of the PPTA fibres occurs in the commonly used short beam shear (SBS) test, i.e. adhesion is no longer the limiting factor in the performance of these fibre-reinforced composites.

**Table 2** Tensile strength and adhesion to epoxy resin for treated and untreated Twaron D1000 aramid fibres

Treatment	Tensile strength (GPa)	Pull-out force <sup>a</sup> (N/mm)	Bundle pull-out shear strength (MPa)
None	2.2	57.4	28.3
Oxalylchloride-water	2.2	76.0	38.3
Oxalylchloride-methanol	2.2	76.6	38.6
Oxalylchloride-ethylenediamine	2.1	84.8	43.0
Oxalylchloride-glycidol	2.1	100.0	52.2

<sup>a</sup>Maximum force recorded divided by the embedded length

SEM-micrographs (to be published elsewhere<sup>12</sup>) show that the fibre surface remains just as smooth after the treatment as it was before. This is consistent with the improved adhesion being caused by the introduction of the functional groups mentioned earlier. Of the different groups introduced, the epoxy groups are by far the most effective. The amine and aldehyde/acid groups, which can also form chemical bonds with the epoxy resin, give smaller improvements in adhesion. In fact, the results are comparable to the results obtained for the PPTA fibres modified with ester groups. These last groups are only capable of hydrogen bonding. This might suggest that the amine and aldehyde/acid groups do not form covalent bonds with the epoxy resin. However, to attribute the improved adhesion to either increased hydrogen bonding or to chemical modification requires a full knowledge of the physicochemical nature of the surfaces, which has not yet been undertaken. Determination of the physicochemical properties and the effect of the surface treatment on composite behaviour (SBS) will be the goal of future work.

In conclusion pull-out tests showed that this newly developed surface treatment procedure markedly improves the adhesion to epoxy resins. Moreover, the improved adhesion is not achieved at the expense of a decrease in tensile strength of the PPTA fibres.

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## Polyethylene adipate spherulites obtained at low supercooling

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Polyethylene adipate ( $M_n$  c. 2000) crystallized isothermally at low supercooling exhibits three spherulitic forms. Depending on the crystallization temperature negative ( $48^\circ\text{C}$ ), positive ( $37^\circ\text{C}$ ) and ring spherulites ( $27^\circ\text{C}$ ) are obtained. A mechanism of ring growth in spherulites is proposed, based on their melting behaviour.

(Keywords: polyethylene adipate morphology; ring spherulites; supercooling)

### Introduction

The ring spherulites found in many polymers, as PE, PA, PP, PTFE, PEA, POM etc. are of particular interest<sup>1-19</sup>. The explanation of the presence of rings has so far been attempted in many ways<sup>9-19</sup>. For example, it was attributed to the spiral twisting of fibrils during growth of spherulites or to the periodic change of orientation of crystallites along the spherulite radius. Teitelbaum<sup>20</sup> suggested for the polyethylene adipate (PEA) a model of rings with  $\alpha$  and  $\beta$  structures alternating with each other. He has found both these forms in the PEA of molecular mass c. 2000. According to his findings ring spherulites exist in the PEA when crystallized isothermally within a temperature range between  $20^\circ\text{C}$  and  $40^\circ\text{C}$ .

At temperatures higher than  $40^\circ\text{C}$  positive needle spherulites are formed. This spherulite consists only of the  $\alpha$  form. At temperatures beneath  $20^\circ\text{C}$  radial optically negative spherulites consisting of  $\beta$  form crystallites are observed. Similar spherulites were obtained by Takayanagi and Jamashito<sup>21</sup>. The existence of an optically negative form not far below  $20^\circ\text{C}$  has not been confirmed by later experiments<sup>22,23</sup>. According to reference 24 the same polymer with molecular mass exceeding 4000 crystallized only in the  $\beta$  form, whereas only the  $\alpha$  form was found in the polymer with molecular mass lower than 800. Because ring spherulites are also obtained in the polymer, polymorphism cannot be the only reason for the occurrence of rings. The present work is an attempt to offer another explanation for the occurrence of ring spherulites in PEA, based on the types of spherulitic forms obtained at low supercooling.

### Experimental

**Material.** Polish manufactured polyethylene adipate (Zachem, Bydgoszcz) was used.

**Samples for optical microscopy.** These were prepared by melting the polymer between two microscope cover glasses for 2 min at c.  $80^\circ\text{C}$ . The samples were crystallized at three different temperatures; 1- $48^\circ\text{C}$ , 2- $38^\circ\text{C}$ , 3- $28^\circ\text{C}$ , and then observed under an optical microscope with crossed polarizers.

**Melting point.** ( $T_m$ ) was determined using the sample subsequently crystallized at  $48^\circ\text{C}$  for three days, at  $38^\circ\text{C}$  for 2 h, finally at  $28^\circ\text{C}$  for 1 h and at  $18^\circ\text{C}$  to the end of crystallization. This sample, showing coexistence of spherulites corresponding to the different crystallization temperatures, was placed under a polarizing microscope equipped with a hot stage (Boetius, DDR). The temperature of the hot stage was then increased at a rate of  $2^\circ\text{C min}^{-1}$ , and the temperatures of birefringence disappearance of different morphological forms were noted.

### Results

At a temperature of  $48^\circ\text{C}$  the optically negative radial spherulites were obtained. Elongated, needle-shaped forms appear along the radius of these spherulites. Spherulites in PEA have not yet been described in the literature. Similar spherulites, but with a different optical sign, crystallize at  $38^\circ\text{C}$ . Crystallization at  $28^\circ\text{C}$ , in turn, gives rise to ring spherulites in which optically positive and negative rings alternate each other. The