Grafting of polyesters onto inorganic fibres by the anionic ring-opening copolymerization of epoxides with cyclic acid anhydrides initiated by potassium carboxylate groups introduced onto the surface

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The grafting of polyesters onto inorganic fibres by the anionic ring-opening copolymerization of epoxides with cyclic acid anhydrides initiated by potassium carboxylate groups introduced onto the surface was investigated. The introduction of potassium carboxylate groups onto inorganic fibres, such as glass fibre and alumina fibre, was achieved by the treatment of the fibre with 4-trimethoxysilyltetrahydrophthalic anhydride followed by neutralization with potassium carbonate. The anionic ring-opening copolymerization of epoxides with cyclic acid anhydrides was successfully initiated by potassium carboxylate groups on the inorganic fibres and the corresponding polyesters were grafted onto the surfaces; the percentage of grafting of polyester from styrene oxide and phthalic anhydride onto glass fibre reached 36.9%.

(Keywords: polyester; fibres; grafting)

INTRODUCTION

The physical properties of fibre-reinforced plastics are known to depend not only on the properties of the matrix polymer and fibre, but also on the adhesiveness of the interfacial regions between the two components[1,2]. To transmit stress from polymer matrix to fibres, the surface modification of fibres by the grafting of polymers has been widely investigated[3–10].

In a series of papers, we reported the grafting of various polymers onto carbon fibre surfaces by the polymerization of monomers initiated by the introduction of initiating groups onto the surface. The initiating groups were successfully introduced onto the fibre surface by using polycondensed aromatic rings and phenolic hydroxyl and carboxyl groups present on the surface. For instance, the anionic graft polymerization of vinyl monomers was successfully initiated by metallized aromatic rings of carbon fibre to give polymer-grafted carbon fibre[5]. Furthermore, by the anionic ring-opening alternating copolymerization of epoxides with cyclic acid anhydrides initiated by potassium carboxylate groups introduced onto the surface, the corresponding polyester was found to be grafted onto carbon fibre[6].

The grafting of polymers onto vapour-grown carbon fibres, i.e. carbon whiskers, was also achieved by use of azo[7], potassium carboxylate[8], and acylium perchlorate groups[9,10] introduced onto the surface. These initiating groups were also introduced by using surface carboxyl and phenolic hydroxyl groups.

In contrast to carbon fibres and carbon whiskers, inorganic fibres, such as glass fibres and alumina fibres, have neither polycondensed aromatic rings nor carboxyl and phenolic hydroxyl groups. Inorganic fibres, however, have surface hydroxyl groups. Therefore, the conversion of the surface hydroxyl groups to initiating groups, by methods different from those used for carbon fibres and carbon whiskers, is required for the effective initiation of graft polymerization from inorganic fibre surfaces.

In the present paper, to modify these inorganic fibre surfaces by the grafting of polyesters, the introduction of potassium carboxylate groups onto the fibre surfaces (*Scheme 1*) and the grafting of polyesters by anionic ring-opening alternating copolymerization of epoxides with cyclic acid anhydrides by use of potassium carboxylate groups introduced onto the surfaces (*Scheme 2*) were investigated.

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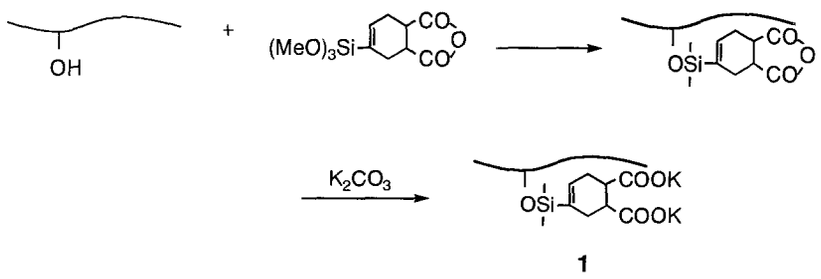
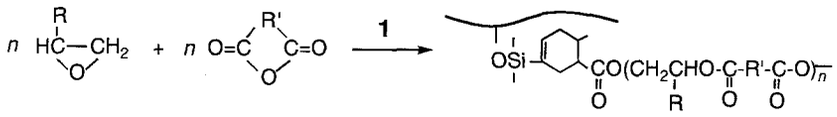


Scheme 1



Scheme 2

EXPERIMENTAL

Inorganic fibres

Glass fibre (E-type) was obtained from Nippon Electric Glass Company Ltd, Japan, and the surface was cleaned by heat treatment. Alumina fibre was obtained from Sumitomo Chemical Industries Company Ltd, Japan, and the surface was also cleaned by heat treatment. The average diameter of the filament, BET specific surface area, and hydroxyl group content of these fibres are shown in *Table 1*. The hydroxyl group content was determined by measuring volumetrically the amount of ethane evolved by reaction with triethylaluminium[11,12].

The inorganic fibres were cut into lengths of about 5 mm, washed with pure water, and dried *in vacuo* at 120°C before use.

Monomers and reagents

Styrene oxide (SO), glycidyl phenyl ether (GPE), glycidyl methacrylate (GMA) and chloromethyloxirane (ECH) were dried over calcium hydride and distilled under reduced pressure. Phthalic anhydride (PAn), maleic anhydride (MAn) and succinic anhydride (SAn) were recrystallized from chloroform or benzene and sublimed under reduced pressure.

m-Xylene and toluene were washed with concentrated sulfuric acid, refluxed over sodium, and distilled. Nitrobenzene was washed with dilute sulfuric acid, dried over calcium chloride and distilled under reduced pressure. Hexamethylphosphoramide (HMPA) was distilled twice under reduced pressure.

4-Trimethoxysilyltetrahydrophthalic anhydride (TSPA) was obtained from Nissan Chemical Company Ltd, Japan, and was used without further purification. 18-Crown-6 and *N*-phenyl-*β*-naphthylamine (NPNA) were obtained from Tokyo Kasei Kogyo Ltd, Japan, and dried *in vacuo* before use.

Introduction of anhydride groups onto fibre surface

To introduce acid anhydride groups onto the glass fibre and alumina fibre surfaces, 3.0 g of fibre was treated with 200 cm^3 of 5% toluene solution with TSPA at 120°C for 8 h. After the treatment, the fibre was filtered and purified by extraction with tetrahydrofuran using a Soxhlet apparatus for 48 h. The resulting fibre was dried *in vacuo* at 120°C.

Table 1 Properties of glass fibre and alumina fibre

Inorganic fibre	Diameter of filament (μm)	BET surface area ($m^2\,g^{-1}$)	OH group content (meq g^{-1})
Glass	1.0	0.41	0.10
Alumina	10.0	0.22	0.53

Determination of acid anhydride groups on the surface

The amount of acid anhydride groups introduced onto the fibre surface was determined by back titration[13]. A typical example was as follows. Into a flask, 0.5–1.0 g of fibre and 20.0 cm^3 of 0.01 N potassium carbonate aqueous solution were charged and the mixture was stirred under nitrogen at room temperature. After 1 h, 10.0 cm^3 of the supernatant solution was pipetted off and treated with 15.0 cm^3 of 0.01 N HCl aqueous solution. Then the solution was titrated with 0.01 N NaOH aqueous solution.

Introduction of potassium carboxylate groups onto the surface

To convert the surface acid anhydride groups on glass fibre and alumina fibre into potassium carboxylate groups, the fibre having acid anhydride groups was treated with an aqueous solution of potassium carbonate. Into a 300 cm^3 flask, 3.0 g of the fibre and 200 cm^3 of 0.1% potassium carbonate aqueous solution were charged. The reaction mixture was stirred at room temperature for 15 min. The treated fibre was filtered, washed with distilled water until the filtrate became neutral, and dried *in vacuo*.

Polymerization procedures

Under dry nitrogen, freshly distilled epoxide (0.02 mol) was added to a flask that contained 0.20 g of fibre, cyclic acid anhydride (0.02 mol), 0.02 g of NPNA, and 0.02 g of 18-crown-6. The reaction mixture was stirred with a magnetic stirrer at 120°C. After a certain time, the content of the flask was poured into a large excess of methanol to precipitate the polyester-containing fibre.

The conversion was determined by the equation:

$$\text{Conversion (\%)} = \frac{\text{Precipitate (g)} - \text{Fibre added (g)}}{\text{Monomer charged (g)}} \times 100$$

Percentage of grafting and grafting efficiency

To isolate polyester-grafted fibre from ungrafted polymer, ungrafted polymer was extracted with chloroform using a Soxhlet apparatus until no more polymer could be extracted with the solvent. Then the polyester grafted onto glass fibre and alumina fibre was determined from the increment of the fibre after the polymerization. The percentage of grafting and grafting efficiency were determined by the following equations:

$$\text{Grafting (\%)} = \frac{\text{Polyester grafted (g)}}{\text{Fibre charged (g)}} \times 100$$

$$\text{Grafting efficiency (\%)} = \frac{\text{Polyester grafted (g)}}{\text{Total polyester formed (g)}} \times 100$$

RESULTS AND DISCUSSION

Introduction of potassium carboxylate groups onto inorganic fibre surface

We reported that potassium carboxylate groups are introduced onto silica surface by the reaction of silica with TSPA followed by treatment with potassium carbonate[14]. Therefore, the introduction of potassium carboxylate groups onto glass fibre and alumina fibre by treatment with TSPA and potassium carbonate was examined.

The amount of potassium carbonate reacted with TSPA-treated glass fibre was determined to be 0.08 meq g^{-1}. On the other hand, TSPA-treated alumina fibre was found to consume 0.05 meq g^{-1} of potassium carbonate. These results indicate that 0.08 meq g^{-1} (0.19 meq m^{-2}) and 0.05 meq g^{-1} (0.23 meq m^{-2}) of potassium carboxylate groups can be introduced onto glass fibre and alumina fibre surfaces, respectively, by the above treatment (as shown in *Table 2*). In spite of the higher hydroxyl group content of alumina fibre, the amount of potassium carboxylate groups introduced onto alumina fibre was almost equal to that introduced onto glass fibre.

The percentage of surface hydroxyl groups on alumina fibre reacted with TSPA (*R* in *Table 2*) was much less than on glass fibre. The surface of alumina fibre is considered to be more porous than that of glass fibre: the fibre diameter of alumina fibre was 10 times that of glass fibre, but the surface area of alumina fibre was only one-half that of glass fibre. Therefore, hydroxyl groups of alumina fibre present in the pores hardly reacted with TSPA because of the steric hindrance. The possibility of neighbouring group effects is present in the reaction of hydroxyl groups on alumina fibre with TSPA.

Table 2 Carboxyl groups introduced onto inorganic fibres

Inorganic fibre	Carboxyl groups (meq g^{-1})	Carboxyl groups (meq m^{-2})	R^a (%)
Glass	0.08	0.19	80.0
Alumina	0.05	0.23	9.4

[a] Percentage of hydroxyl groups reacted with TSPA

Table 3 Copolymerization of SO with PAn in the presence of glass fibre[a]

Glass fibre	SO (mol)	PAn (mol)	Conversion (%)	Grafting (%)
None	0.02	0.02	0	–
Untreated	0.02	0.02	0	–
GF-COOK[b]	0.02	–	0	–
GF-COOK[b]	–	0.02	0	–
GF-COOK[b]	0.02	0.02	82.4	34.6

[a] Glass fibre, 0.20 g; 18-crown-6, 0.02 g; NPNA, 0.02 g; 120°C; 3 h
[b] Glass fibre having potassium carboxylate groups

Copolymerization of SO with PAn initiated by potassium carboxylate groups on glass fibre

It has been reported that alkali metal carboxylates, such as sodium acetate, initiate the anionic ring-opening copolymerization of epoxides with cyclic acid anhydrides to give the corresponding polyesters[15]. We succeeded in grafting polyesters onto carbon black[16,17], carbon fibres[6], carbon whiskers[8], and silica[14] by the copolymerization of epoxides with cyclic acid anhydrides by means of potassium carboxylate groups introduced onto these surfaces.

Therefore, the initiating activity of potassium carboxylate groups introduced onto glass fibre (GF-COOK) for the ring-opening copolymerization of SO with PAn was examined under several conditions. The results are shown in *Table 3*. In the polymerization, 18-crown-6 was added to accelerate the anionic copolymerization[18]. NPNA was also added in the reaction mixture as an inhibitor of radical polymerization, because the thermal polymerization of SO with PAn proceeded at a high temperature.

As seen in *Table 3*, the ring-opening copolymerization of SO with PAn could not be detected in the absence of glass fibre or in the presence of untreated glass fibre. Neither SO nor PAn alone was polymerized by potassium carboxylate groups on glass fibre. On the contrary, when equimolecular amounts of SO and PAn were heated at 120°C, the ring-opening copolymerization was initiated in the presence of GF-COOK to give the corresponding polyester, i.e. poly(SO-*alt*-PAn); the structure was identified by i.r. and ^{1}H n.m.r.

Figure 1 shows the time–conversion curves in the ring-opening copolymerization of SO with PAn or SAn initiated by potassium carboxylate groups on glass fibre. *Figure 1* clearly shows that the ring-opening copolymerizations of SO with PAn or SAn are successfully initiated by glass fibre having potassium carboxylate groups. In the polymerization, an induction period of about 1 h was observed. Such an induction period was often observed in the polymerization initiated by initiating groups introduced onto powder and fibre surfaces[6,8].

Evidence of polyester grafting onto glass fibre surface

Figure 2 shows the relationship between reaction time and percentage of polyester grafting onto glass fibre obtained from the copolymerizations shown in *Figure 1*.

As shown in *Figure 2*, the percentage of polyester grafting increased with the progress of polymerization to 26.0–36.9%. This indicates that the ring-opening polymerization is initiated by potassium carboxylate groups introduced onto glass fibre, and grafted chains

are propagated from the surface to give polyester-grafted glass fibre (*Scheme 2*).

On the other hand, the grafting efficiency of polyester was relatively high at the initial stage of polymerization, but decreased to a few per cent with the progress of polymerization, as shown in *Figure 3*. This indicates that ungrafted polymer is gradually formed by a chain transfer reaction of growing polymer anion with a trace of carboxylic acid and water (HB), as shown in *Scheme 3*.

Figure 4 shows the difference *FT*i.r. spectrum between untreated and poly(SO-*alt*-PAn)-grafted glass fibre. The i.r. spectra agreed with polyester synthesized from SO with PAn by use of potassium acetate as a catalyst.

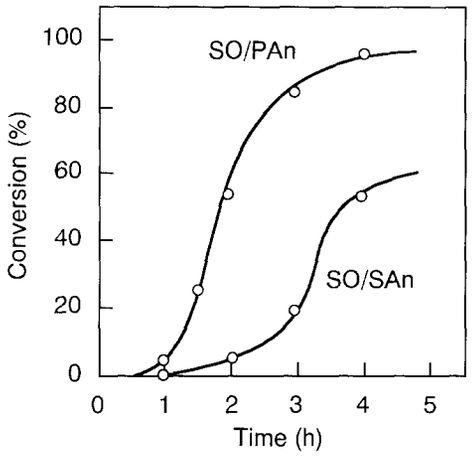


Figure 1 Anionic ring-opening copolymerization of SO with PAn or SAn initiated by potassium carboxylate groups introduced onto glass fibre. Glass fibre, 0.20 g; epoxide = anhydride = 0.02 mol; 18-crown-6, 0.02 g; NPNA, 0.02 g; 120°C

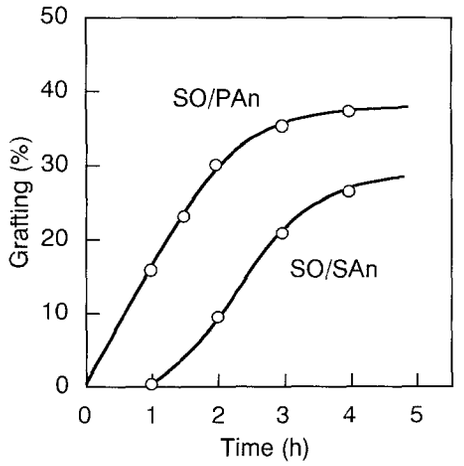


Figure 2 Relationship between reaction time and percentage of polyester grafting onto glass fibre. Polymerization conditions are as given in *Figure 1*

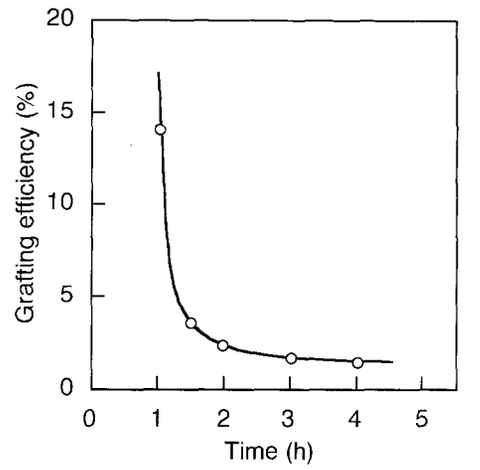


Figure 3 Relationship between reaction time and grafting efficiency of polyester from SO and PAn. Polymerization conditions are as given in *Figure 1*

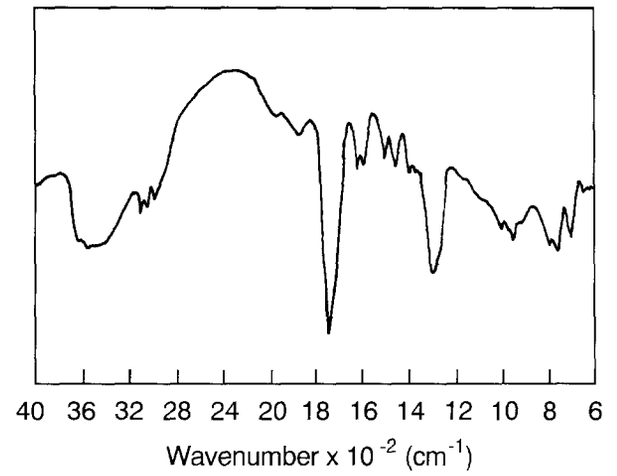
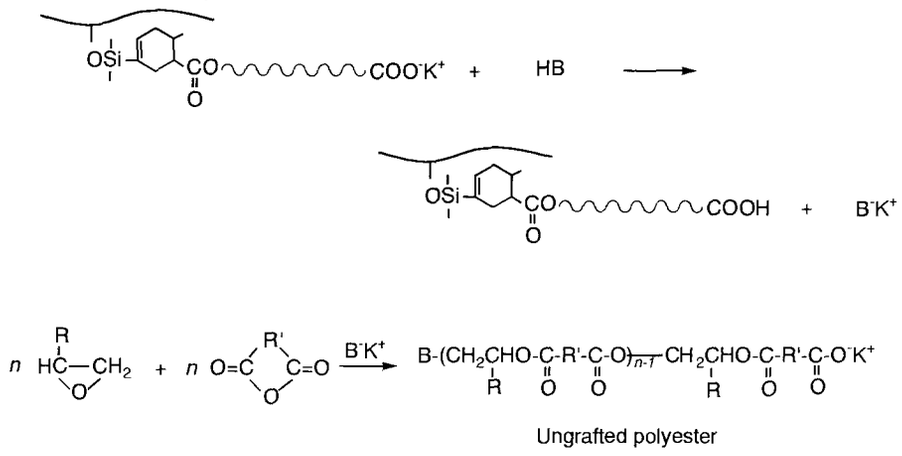


Figure 4 Difference *FT*i.r. spectrum between untreated and poly(SO-*alt*-PAn)-grafted glass fibre



Scheme 3

Table 4 Grafting of several polyesters onto glass fibre[a]

Epoxide	Anhydride	Time (h)	Conversion (%)	Grafting (%)	Grafted polymer ($g\,m^{-2}$)
SO	PAn	4	96.0	36.9	0.90
SO	SAn	4	52.3	26.0	0.63
SO	MAn	9	25.2	24.9	0.59
ECH	PAn	40	38.8	28.2	0.69
GPE	PAn	40	54.9	26.6	0.65
GMA	PAn	4	38.3	gelation	–

[a] Glass fibre, 0.20 g; epoxide = anhydride = 0.02 mol; 18-crown-6, 0.02 g; NPNA, 0.02 g; 120°C

Table 5 Grafting of several polyesters onto alumina fibre[a]

Epoxide	Anhydride	Time (h)	Conversion (%)	Grafting (%)	Grafted polymer ($g\,m^{-2}$)
SO	PAn	3	14.1	18.8	0.85
SO	SAn	4	11.6	20.0	0.91
SO	MAn	9	29.6	13.4	0.61
ECH	PAn	40	18.6	15.3	0.68
GPE	PAn	30	66.6	11.7	0.53

[a] Alumina fibre, 0.20 g; epoxide = anhydride = 0.02 mol; 18-crown-6, 0.02 g; NPNA, 0.02 g; 120°C

Table 6 Effects of crown ether and solvent on the polyester grafting[a]

Crown ether	Solvent	Time (h)	Conversion (%)	Grafting (%)
None	None	3	40.7	10.2
18-Crown-6	None	3	82.4	34.6
None	*m*-Xylene	9	14.4	5.7
None	Nitrobenzene	9	29.6	27.5
None	HMPA	9	67.2	8.6

[a] Glass fibre, 0.20 g; SO = PAn = 0.02 mol; solvent, 3.0 cm^3; NPNA, 0.02 g; 120°C

The mass average molecular weight of ungrafted polyester, poly(SO-*alt*-PAn), was determined to be 7800 ($M_w/M_n = 1.35$) by g.p.c. using polystyrene standards.

Grafting of several polyesters onto glass fibre surface

The ring-opening copolymerization of several epoxides with cyclic acid anhydrides was carried out and the grafting of polyesters onto glass fibre was evaluated. The results are summarized in *Table 4*. It is apparent from *Table 4* that potassium carboxylate groups on glass fibre have an ability to initiate the ring-opening copolymerization of epoxides with cyclic acid anhydrides, and various polyesters can be grafted from the surface, based on the propagation of polyester from the surface.

Grafting of several polyesters onto alumina fibre surface

The grafting of several polyesters onto alumina fibre by the anionic ring-opening copolymerization of epoxides with cyclic acid anhydrides by use of potassium carboxylate groups introduced onto the surface was examined. The results are summarized in *Table 5*. As seen in *Table 5*, potassium carboxylate groups introduced onto alumina fibre also have an ability to initiate the ring-opening copolymerization of epoxides with cyclic acid anhydrides to give the corresponding polyester-grafted alumina fibre. The amount of grafted polyester onto alumina fibre per square metre was found to be almost equal to that of glass fibre.

Effects of crown ether and solvent on the grafting

It is well known that the anionic polymerization is remarkably accelerated by the addition of crown ether[18–20]. *Table 6* shows the effect of 18-crown-6 on the ring-opening copolymerization of SO with PAn initiated by potassium carboxylate groups on glass fibre. As shown in *Table 6*, it was found that the addition of crown ether is very effective to increase the polymerization rate and to obtain polyester-grafted glass fibre with a higher percentage of grafting. This may be due to the stabilization of countercation by 18-crown-6.

Furthermore, it became apparent that the rate of ring-opening copolymerization increases, depending on the solvent, in the following order: *m*-xylene < nitrobenzene < HMPA. This corresponds to the order of increasing dielectric constant of the solvent. This is due to the fact that HMPA solvates the countercation to give solvent-separated ion pairs. This accelerates the copolymerization rate.

On the other hand, the percentage of polyester grafting decreased in HMPA. This suggests that in HMPA, chain transfer reaction of growing polymer anion proceeded preferentially.

CONCLUSIONS

Potassium carboxylate groups were introduced onto glass fibre and alumina fibre surfaces by treatment of the surface with TSPA followed by reaction with potassium carbonate.

The anionic ring-opening copolymerization of epoxides with cyclic acid anhydrides was successfully initiated by the surface potassium carboxylate groups to give the corresponding polyester-grafted fibre.

The addition of 18-crown-6 into the copolymerization system is effective to obtain polyester-grafted fibre with a higher percentage of grafting.

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