Polyvinylpyridine–divinylbenzene and asbestos composites

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The *in situ* copolymerization of vinylpyridine and divinylbenzene in crysotile asbestos cardboards yields composites of higher mechanical strength and chemical stability than plain carboard. The composites have been tested as gasket rings and separators of advanced alkaline water electrolysers. The chemical and morphological changes to which the materials are subjected under these conditions have been followed up by i.r. spectroscopy and SEM and correlated with chemico-physical properties.

(Keywords: polymerization; polyvinylpyridine–divinylbenzene; asbestos; separator; electrolysis; gaskets)

INTRODUCTION

Natural hydrated polysilicates, with the generic name 'asbestos', are unique minerals combining unusual physical and chemical properties. In the form of fibres, these materials fulfill a wide variety of industrial applications[1]. The electrochemical industry conventionally uses crysotile asbestos cardboards and cloth as first choices for use as sealing gaskets or to separate the positive and negative electrolytes (batteries[2], chloro-alkali[3], water[3,4], electrolysis cells). The reason for this lies in the fact that no other natural or synthetic material matches the desirable combination of thermal and chemical stability, mechanical strength and flexibility, as well as the wettability and affinity for polar molecules which is offered by crysotile asbestos.

With the advent and growth of the 'energy crisis', higher demands have been made of this material. During hydrogen production by advanced alkaline water electrolysis[5] traditional asbestos separators fail[6] at $T > 100°C$ due to insufficient mechanical strength and to their chemical deterioration:

$$Mg_3Si_2O_5(OH)_4 + KOH\ (aq) = 3\,Mg(OH)_2 + \text{soluble silicates (aq)} \qquad (1)$$

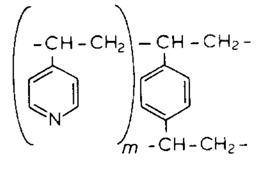
The identification of stable, electrically conductive materials to work in hot ($T \geqslant 120°C$) concentrated alkali (KOH 30–50% w/w) is currently a major objective of large international organizations, such as the European Economic Community and the International Energy Agency, who aim to use hydrogen as an energy carrier[5]. In this context we have undertaken a systematic study of alkali resistant organic polymers to reinforce asbestos cardboards against the chemical environment and mechanical wear in advanced water electrolysers. The polymers belong to two classes: aromatic polymers, such as polyphenylenes[7,8], and aliphatic polymers carrying aromatic substituents, such as polyphenyl-ethylenes[9].

As far as the mechanical and chemical protection of asbestos is concerned, the success of the above approach depends on the extent and uniformity of the asbestos cardboard fibres (the alkali resistant organic polymer). Each of the above inorganic–organic composite polymeric materials presents specific synthetic features.

A second, important, aspect is the material's wettability and porosity, which determines its surface specific electrical resistance. Generally, asbestos cardboards should not be heavily loaded with non-wettable organic polymers (e.g. polyphenylenesulphide[7,8] or polystyrene–divinylbenzene[9]) in order to retain sufficient porosity and maintain satisfactory electrical conductivity. Sulphonation[7,9] of the organic polymer provides the composite material with a higher wettability which overcomes the negative effect of lower porosity on electrical conductivity.

Vinylpyridine polymers[10] (which contain highly polar pyridine nuclei) have a wide range of applications, some of the most interesting of which are based on their ability to act as polyelectrolytes. The crosslinked vinylpyridine (VP)—divinylbenzene (DVB) copolymers (VP–DVB) are insoluble and have applications as ion exchange polymers at high temperatures[11]. The 4-VP–DVB copolymer containing 10% mole/mole of DVB, has been reported[12] to produce ion-exchange resins which resist prolonged treatment with strong acidic alkali solutions at 100°C.

The full potential of these materials has not yet been realized. We report in this paper the *in situ* synthesis of one of these materials (I) and the properties of the composite materials made out of this copolymer and asbestos*.



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* Previous communications given[13].

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EXPERIMENTAL

Materials and preparations

The manufacture of the VP–DVB–asbestos cardboards has been accomplished according to a general procedure[14] described previously[9]. Commercially available (APC-CAT, Milan) Canadian crysotile asbestos cardboards (0.055 cm thick) were soaked at 0°C in acetone containing varying concentrations of freshly distilled vinylpyridine, 50% divinylbenzene in (ethylbenzene) and benzoylperoxide (BP) catalyst. This mixture was removed from the bath, heated to 70°C, washed with acetone and dried to determine the cardboard weight gain. (The reagents (Fluka) mole ratios were $VP/DVB = 9$ and $BP/(VP + DVB) = 0.01$.)

Samples of VP–DVB were obtained by carrying out the copolymerization of VP and DVB at room temperature in the absence of solvent (bulk polymerization), and also in a 25% monomer solution in acetone (solution–suspension polymerization). The reaction time was of the order of several weeks; after this length of time the bulk polymerization samples were very hard, compact solids. In the solution–suspension reaction the monomers were completely soluble initially, but more solid formed as the reaction proceeded. The copolymer in this case was of the macroporous type[11,15] and much easier to grind. At the end of the reaction time the ground solids were washed with acetone in Soxlet extractors for 24 h and dried for 4 h at 120°C.

Characterization

I.r. SEM scans, liquid regain and tensile strength measurements have been obtained previously[9]. From the i.r. spectra of freshly made ground cardboards the net absorbances $\bar{A}_{3695}$ and $\bar{A}_{960}$ of the asbestos bands and $\bar{A}_{1420}$ of the VP–DVB band were obtained by subtracting the absorbance (A) $3470\ \mathrm{cm}^{-1} - 3695\ \mathrm{cm}^{-1}$, $860\ \mathrm{cm}^{-1} - 960\ \mathrm{cm}^{-1}$, and $1400\ \mathrm{cm}^{-1} - 1420\ \mathrm{cm}^{-1}$. The absorbance ratio $R_A = \bar{A}_{1420}/\bar{A}_{960}$ correlated well (correlation coefficient $\rho = 0.96$) with the cardboard weight ratio R_w (cardboard weight gain/plain cardboard weight) according to Beer's law,

$$R_A = a\,R_w \qquad (2)$$

where the 1420–960 bands absorptivity ratio (a) is 0.336. Equation (2) was used to determine the surface area of the cardboard and the cross-sectional VP–DVB concentration ($C_1\%\ \mathrm{w/w} = R_w 100/(R_w + 1)$) from R_A values obtained in the i.r. spectra of the KBr pellets. The samples had been removed from the surface (and the cross-section) of the cardboard in its original physical form. All other experimental details have been previously described[8].

RESULTS AND DISCUSSION

From the three best known methods for making composites (i.e. mechanical mixing, casting from a common solvent, and polymerization of one monomer in the presence of the other polymer) we chose the *in situ* copolymerization of 4-VP and DVB onto an asbestos polysilicate phase. The chemical and physical properties of the inorganic[1] and organic[10] polymeric constituents of the asbestos–VP–DVB composites make the other techniques impractical or non-applicable. In addition the *in situ* copolymerization allows the use of crysotile asbestos cardboards which are commercially available and fit any electrochemical cell.

The porous 0.005 cm thick asbestos cardboards, which were used, exhibit a considerable liquid regain (0.4 ± 0.05 w/w) when equilibrated with solvents of different polarity, ranging from H_2O to toluene. Thus an easy method of transferring and uniformly distributing 4-VP and DVB monomers into the asbestos phase, is to soak the cardboard with the monomers dissolved in a suitable solvent (e.g. acetone). The polymerization of the monomers sorbed into the cardboard is then accomplished[9] simply by withdrawing the cardboard from the soaking bath and raising the temperature to 70°C. Under these experimental conditions the cardboard weight gain ($10 \leqslant C_1\ \%\,\mathrm{w/w} \leqslant 24$), as determined after polymerizing the monomers, washing with acetone and drying, depends on the total monomer concentration ($25.8 \leqslant C_M\,\%$ w/w 54.2) in the soaking bath: $C_1 = 0.48\ C_M - 2.15$ (3) ρ (correlation coefficient) = 0.998. This technique has previously been shown[9] to yield crosslinked polymers (e.g. polystyrene–divinylbenzene) characterized by a high degree of internuclear chain entanglement and similar to those obtained by bulk copolymerization[9,16]. Although initially the monomers are sorbed by the porous cardboards in the diluted acetone solutions, at 70°C the solvent evaporates from the polymerization phase and the reaction proceeds in the presence of the unreacted monomers (as solvents).

The i.r. spectra (see *Figure 1*) of the composite materials exhibited the band patterns of asbestos (bands at 3695, 3420, 1070, 1020 and $960\ \mathrm{cm}^{-1}$)[8] and of polyvinylpyridine–divinylbenzene (bands between 3020 and 1150 and at $820\ \mathrm{cm}^{-1}$). Absorption frequencies and relative intensities of each band pattern are identical to those which were found for the plain commercial cardboard and for the authentic (bulk or macroporous) organic polymer respectively.

The composite materials were stable up to 250°C, in air. Strong exothermic phenomena start above 250°C mainly because of the oxidative degradation[9] of the organic copolymer (see the d.s.c. traces in *Figure 2*). The t.g.a. traces in *Figure 2* show that the initial cardboard weight gain (C_1) is entirely lost between 250°C and 500°C. The i.r. spectra of the thermally degraded materials contained the bands of asbestos only.

From the point of view of investigating the organic copolymer structure, the X-ray powder pattern of the cardboards was of little use, as those of the authentic bulk or macroporous amorphous polymers. The only signals that showed up in the X-ray diffraction pattern of the VP–DVB–asbestos cardboards were those of asbestos which were identical to those of the plain cardboard.

The distribution (surface and cross-sectional concentrations as determined by i.r. spectroscopy) of the organic polymer throughout the asbestos matrix is given in *Table 1*.

From the morphological point of view, the surface (*Figure 3*) and cross section (*Figure 4*) micrographs of plain asbestos and of the VP–DVB–asbestos specimen, show that the fibre bundles and networks of asbestos are not as readily visible in the micrographs of the composite, and that the latter structure is more compact and less porous than the former.

All together the data show that the *in situ* polymeri-

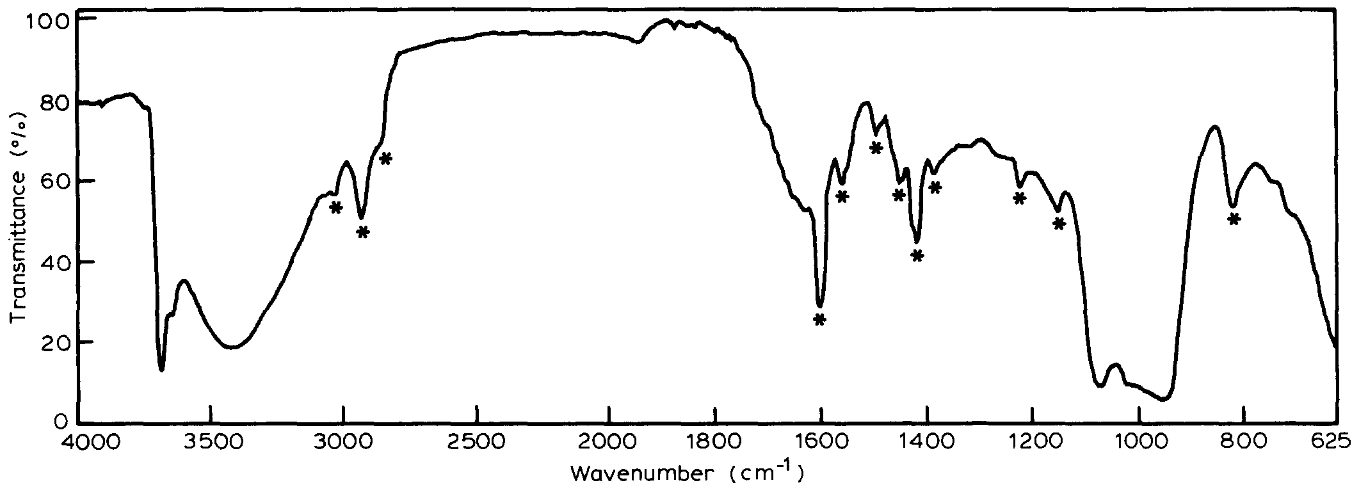

Figure 1 I.r. spectrum of VP–DVB (41% w/w)–asbestos cardboard

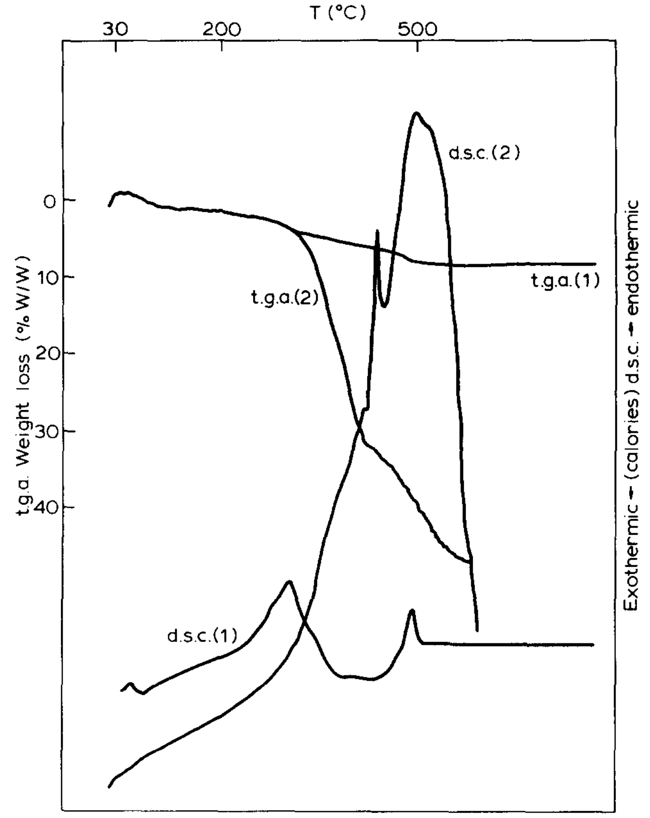

Figure 2 T.g.a.–d.s.c. scans of VP–DVB (41% w/w)–asbestos (2) and plain asbestos (1) cardboards in air at 600°C/h

zation of sorbed VP–DVB monomers leads to the growth of the organic copolymer within the asbestos phase and around the polysilicate fibre bundles in uniformly distributed amounts throughout the cardboard. The insoluble, thermally stable crosslinked copolymer does not appear to differ significantly from the authentic copolymer. The above characterization techniques do not allow us, however, to establish if the *in situ* obtained VP–DVB copolymer is of the bulk or macroporous type. Regardless of this fact, the *in situ* technique described here is so flexible that the concentration (and/or eventually the crosslinking degree) of the organic copolymer in the composite material may be varied over a wide range simply by varying the concentration (and/or eventually the VP/DVB ratio) in the soaking bath.

The availability of composites containing variable concentrations of VP–DVB allows improved investigation of the chemical and physical properties of these materials and some structure–properties relationships. These are significant from the points of view of fundamental knowledge and applied science when dealing with the chemical and physical properties of porous VP–DVB–asbestos composites, one must consider that the changes which occur on varying the organic to inorganic polymer ratio are both chemical and morphological, i.e. the material hydrophilic–lipophilic balance (HLB)* and porosity changes respectively. For instance, filling the void volume of the plain cardboard with the organic polymer yields specimens with higher mechanical strength (*Figure 5*, curve A). The same morphological change is responsible for the decrease of the liquid uptake by the cardboard with increasing VP–DVB concentration (*Figure 6*, curves C and D). However, the different water and toluene ratios (obtained at equal VP–DVB contents) demonstrate that the liquid uptake is not solely governed by the physical dimensions of the porous absorbing structure and permeant molecules; but the interactions of the permeant molecules with the pore walls of the absorbing structure are also very important. Whereas plain asbestos absorbs more water than toluene (sorbed water to toluene ratio $= X = 1.2$), the more lipophilic VP–DVB–asbestos materials exhibit opposite behaviour ($X = 0.5$).

For some applications which require thermal and chemical stability and mechanical strength only (e.g. in the case of sealing gaskets to be used in hot strong alkaline environment) the material's HLB is not important. In other purposes, such as the case of electrolytic separators[2–5], the chemical nature of the material is of supreme importance, since a low hydrophilicity is expensive in terms of high voltage drop across the separator[1,7].

Other important aspects (when performing research work concerning the stabilization of asbestos in the environment of medium temperature alkaline electrolysis) are related to the mechanism of asbestos failure. Generally, under these experimental conditions, asbestos is subjected to strong hydrolytic attack by the alkali and, simultaneously, to a good deal of mechanical erosion induced by the formation of gas pockets in the separator[6].

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* The ratio of water wettable to hydrocarbon-like material in the composite.

These actions are even more severe when operating under pressure and with electrodes pressed against the separator to decrease the operating voltage[18]. High H_2 and O_2 concentrations may develop locally over the separator and demand even higher chemical and mechanical performance of the material.

Chemical and mechanical effects can be discriminated by carrying out long term stability and performance tests at $T \geqslant 120°C$ in 30–50 % w/w KOH under static and dynamic conditions. In the former, the material is only exposed to the chemical action of the boiling alkali[6,8]. In the dynamic tests the material is used as separator in microcells[19] which are assembled according to the principle and design of future advanced alkaline water electrolysers. This equipment enables testing the combined action of chemical attack (by the electrolyte and evolving gases), and mechanical stress caused by pressure and gas evolution in the immediate vicinity of the separator.

Table 1 Distribution of VP–DVB in asbestos cardboards

C_1*	C_s*	C_{cs}*
7.5	7.4	7.8
9.5	9.0	10.8
10.0	12.3	7.9
15.0	14.5	15.0

* VP–DVB % w/w : C_1 by the overall cardboard weight gain, C_s and C_{cs} surface and cross–v sectional concentrations by i.r. spectroscopy

The results of the chemical stability tests for composites containing up to 17% w/w VP–DVB are shown in *Table 2*. The material losses (9–10% w/w) of the VP–DVB–asbestos cardboards are much lower than that (32% w/w) of plain asbestos. Accordingly the former cardboards did not exhibit any visible damage and the latter was swollen and heavily damaged. A dramatic change of chemical composition corresponds to the severe weight loss of the plain cardboard. The MgO/SiO_2 mole ratio initially shifts from 1.5, (identifying[1] the crysotile variety of asbestos), to 5.3. A large excess of MgO is present over the stoichiometric requirement of the initial $Mg_3Si_2O_5$ composition ($MgO/Mg_3Si_2O_5 = 7.6$). This fact agrees with previous observations based on Debye–Scherrer powder patterns which indicated that the deterioration of asbestos in hot KOH (reaction (1)) leads to leaching of silicon from the asbestos and an increasing concentration of the brucite phase in the insoluble residue[6]. In the VP–DVB–asbestos specimen the asbestos chemical composition change and the overall material weight loss are much more limited. The extent of this chemical change seems to attenuate the alkali exposed composites of higher VP–DVB content: $MgO/Mg_3Si_2O_5$ from 1.0 to 0.5 at 6 to 17% VP–DVB.

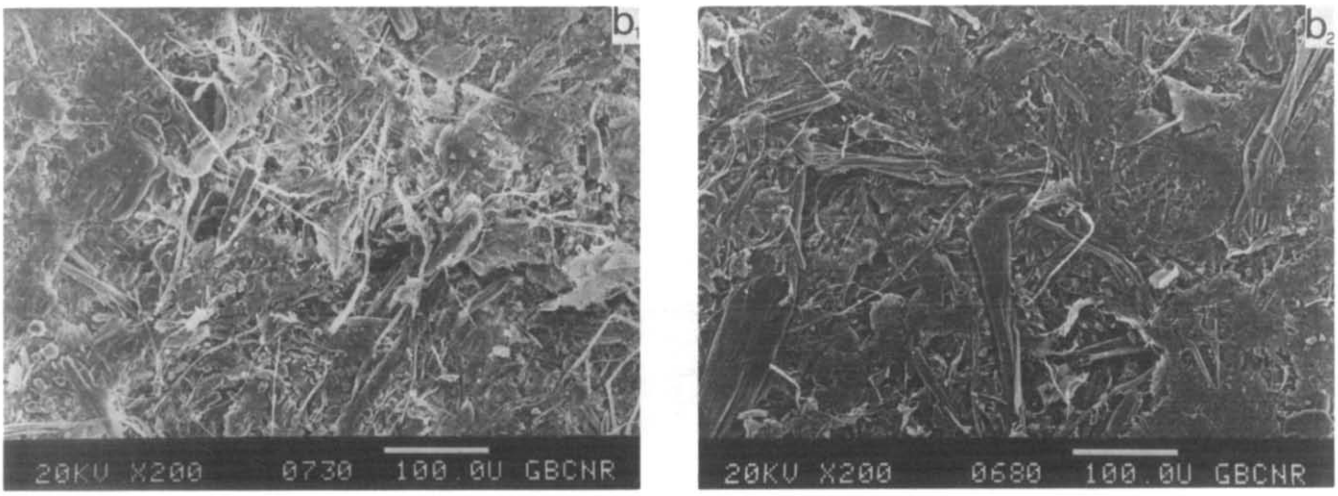

Figure 3 Surface SEM micrograph of plain asbestos (b_1) and VP–DVB (14% w/w)–asbestos (b_2): untreated samples

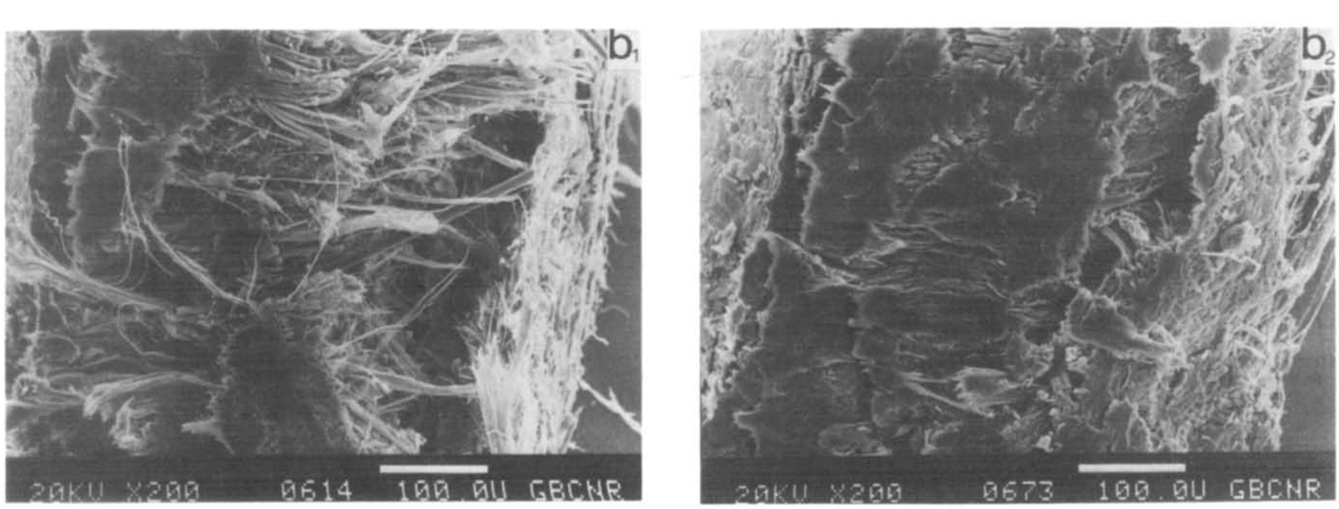

Figure 4 Cross-sectional SEM micrograph of plain asbestos (b_1) and VP–DVB (14% w/w)–asbestos (b_2): untreated samples

The degree of the magnesium polysilicate structure hydrolysis changes the i.r. band pattern of this constituent (see *Figure 7*) accordingly. Macroscopic changes[8] result in a relative increase of chain and/or terminal hydroxyl groups ($\nu_{Si(Mg)OH} = 3695$) and of MgO bonds (broad band covering the 300–600 cm^{-1} range in *Figure 7a*) at the expense of the chain Si–O bonds (bands at 1100–950, 600 and 500–400 cm^{-1}). *Table 2* shows that higher Si(Mg)O–H to Si–OSi(Mg,H) i.r. absorbance ratios correspond to higher MgO/SiO_2 mole ratios (and therefore to more pronounced shifts of equation (1) to the right).

However, no change could be confirmed in the VP–DVB band pattern itself after exposure of the cardboard to the alkali. An increase in the VP–DVB:asbestos bands absorbances ratio was observed however at the end of the chemical stability tests. This ratio was not converted into concentration values since the chemical change induced by the alkali in the cardboard polysilicate component does not warrant indiscriminate application of the absorbance to concentration conversion (equation (2) in the Experimental section). The weight losses of the cardboard between 250° and 500°C (as measured by thermal gravimetric analysis) correspond to the cardboard initial weight gain (C_1) which are independent from the exposure to the alkali. In the cardboards which had been exposed to the alkali, however, the weight loss started at higher temperature (300°C) than in the untreated samples (260°C).

Morphologically, the *SEM* micrographs of the plain asbestos after exposure to the alkali (*Figures* $8b_1$ and $9a_1$) reveal extensive destruction of the initial fibres network, presence of pulverized meterial and higher void fraction. On the contrary the micrographs of the VP–DVB–asbestos specimen at the end of the stability test (*Figures*

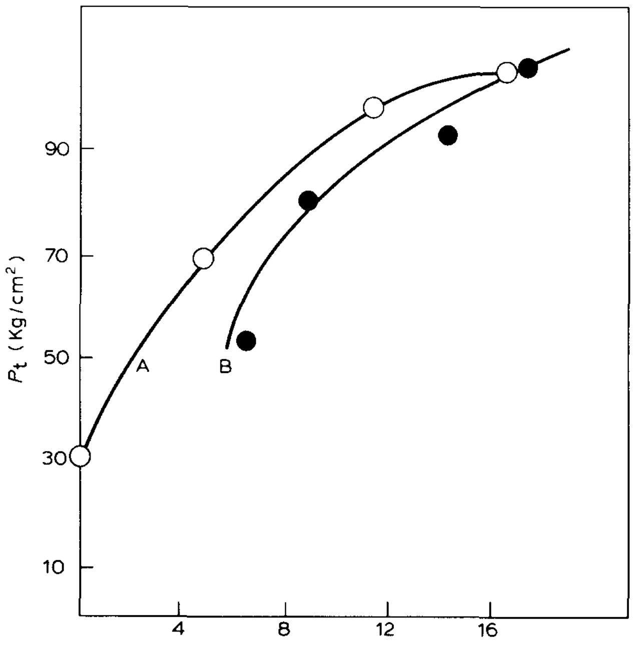

Figure 5 Dependence of tensile strength (P_t) on VP–DVB concentration in asbestos cardboards: curve A, untreated; and curve B, after 2500 h exposure to boiling 30% w/w KOH

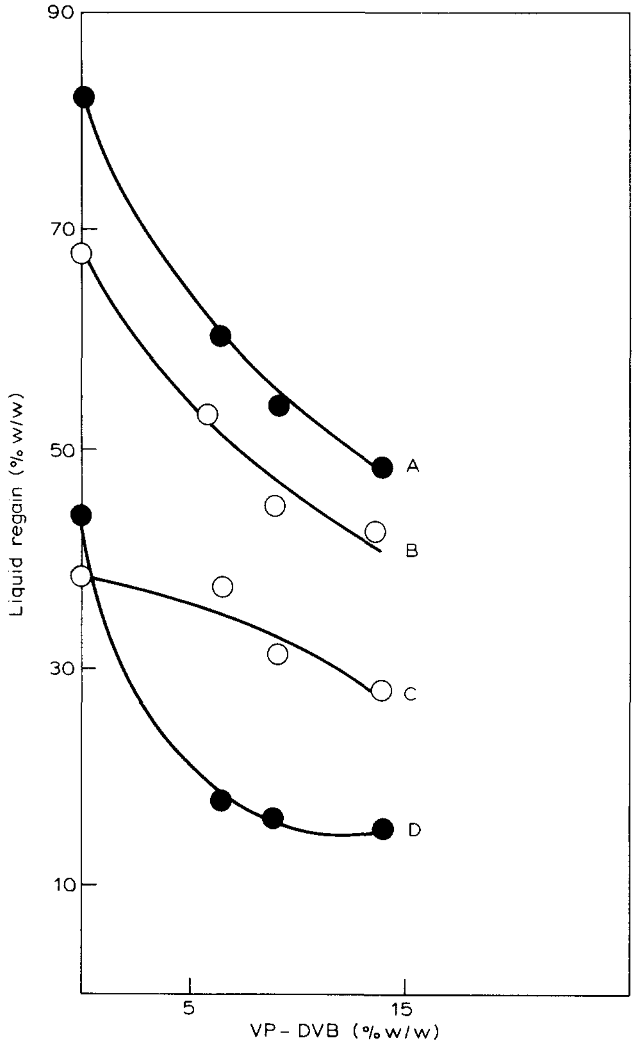

Figure 6 Dependence of toluene (○) and water (●) regain (w/w = sorbed liquid/dry cardboard) on VP–DVB concentration in untreated asbestos (curves C and D) and aged (2500 h in boiling 30% KOH: curves A and B) cardboards

Table 2 Chemical stability tests for VP–DVB–asbestos cardboards in boiling 30% w/w KOH: data obtained before (b) and after 2500 h (a) exposure

C_1%w/w	$\bar{A}_{3695}/\bar{A}_{960}$		Weight loss (%w/w)	MgO%w/w		SiO_2%w/w		MgO/SiO_2 (mole/mole)	
b	b	a	a	b	a	b	a	b	a
nil+	0.50	1.72	32.2	34.2	45.1	34.2	12.8	1.5	5.3
6.4	0.50	0.65	9.8	32.0	33.5	31.8	24.9	1.5	2.0
8.7	0.53	0.55	9.4	31.0	32.3	30.9	23.6	1.5	2.0
14.2	0.52	0.56	9.4	29.8	29.5	30.0	23.0	1.5	1.9
16.6	0.47	0.44	9.9	29.5	28.2	29.0	24.1	1.5	1.7

* VP–DVB concentration by the weight gain; + plain asbestos

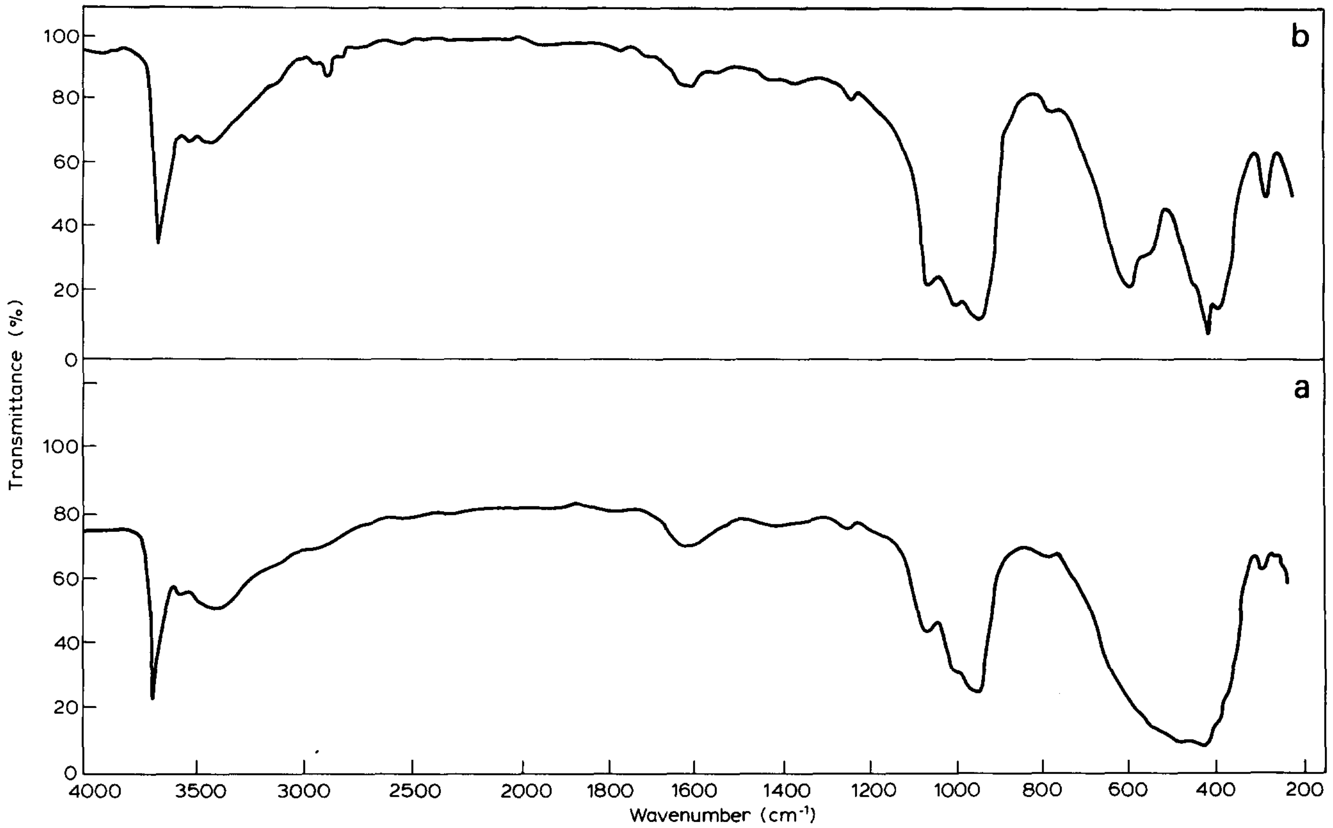

Figure 7 I.r. spectra of plain asbestos before (b) and after (a) 2500 h exposure to boiling 30% KOH

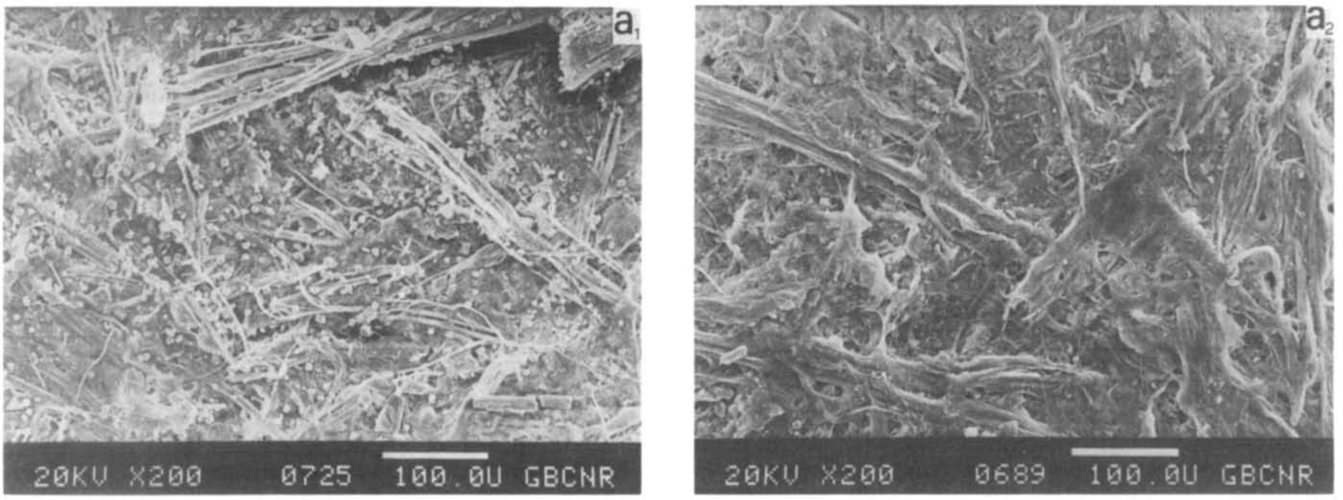

Figure 8 Surface SEM micrographs of plain asbestos (a_1) and VP–DVB (14% w/w)–asbestos (a_2) after 2500 h exposure to boiling 30% KOH

$8b_2$ and *$9b_2$*) do not differ as much from those of the same separator before exposure to the potash (*Figures Cb_2* and *$4b_2$*).

The data confirm that a significant improvement in the asbestos chemical stability is obtained when its fibres are coated with the organic copolymer. The limited weight loss of the reinforced cardboards somehow increases the material porosity, but it does not appear to involve a change of the cardboards' relative VP–DVB contents. The only evident chemical change is related to the structure of the inorganic constituent itself which appears somewhat richer in magnesium, poorer in silicon and to contain a higher concentration of terminal OH functions. The reason for the higher stability toward thermal degradation, which is exhibited by the organic constituent, is not clear at the moment.

The above morphological and chemical modifications do not fail to produce corresponding changes in chemical and physical properties. As a result of weight loss, some decrease in mechanical strength is observed (*Figure 5*, curve D), which increases at lower VP–DVB concentrations. The liquid regain (*Figure 6*, curves A and B) rose as expected. However, it is interesting that the sorbed water:sorbed toluene ratio rose to the point that (contrary to the initial samples) the VP–DVB–asbestos specimen (after exposure to the alkali) absorbed more water than toluene ($X = 1.2$–1.5). This in undoubtedly the effect of the material's HLB shifting to the hydrophilic side caused by

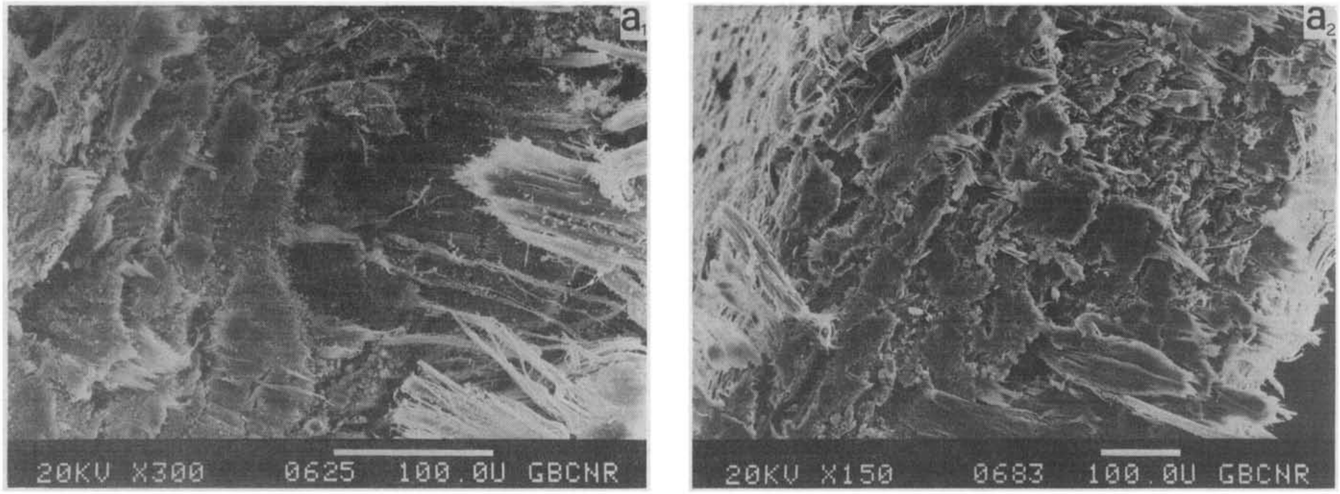

Figure 9 Cross-sectional SEM micrographs of plain asbestos (a_1) and VP–DVB (14% w/w)–asbestos (a_2) after 2500 h exposure to boiling 30% KOH

Table 3 Experimental conditions and results of microcell[19] test at 1 A/cm^2 current density on VB–DVB (11%w/w)–asbestos sealing gaskets and separators

	Experimental conditions					Weight	
Run	KOH (%w/w)	T (°C)	P (bars)	t (h)	Use	loss (%w/w)	R_s (Ω . cm^2)
a	40	90–110	1	3000	gasket ring	50	–
b	50	90–110	1	600–1200	separator	58.5	Fig. 10, 11
c	50	165	20–35	660	gasket ring	40	–

the hydrolytic cleavage of the host magnesium polysilicate phase and the relative increase in the concentration of hydrophilic OH functions.

The effect of loading the asbestos with VP–DVB leads to a significant rise of the cardboard's electrical resistance (from 0.08 for plain asbestos to 0.35 Ω cm^2 for 6–14% VP–DVB–asbestos at 100°C in 30% w/w KOH). The effects of VP–DVB concentration and the alkali treatment on the cardboard's electrical resistance (R_s) are not as obvious, as on the mechanical strength and liquid regain. Across the 6–14% C_1 range and independently of the alkali treatment, R_s in 30% 100°C KOH was 0.35 ± 0.08 Ω cm^2. The morphological and chemical changes, which occur in the cardboard during the alkali treatment, may not be large enough to affect the electrical resistance. The larger morphological changes which occur in the cardboards tested under electrolysis do significantly lower the separator resistivity (as shown later). A similar explanation may be sufficient to explain the lack of any effect of VP–DVB concentration within the $6 \leqslant C_1 \leqslant 14$ range. At 41% w/w VP–DVB content R_s was found very high (8 ± 0.5 Ω cm^2). In order to investigate the effects of C_1; separators of VP–DVB content varying between 14 and 40% w/w should be tested. These heavily loaded separators, of course, are less interesting from the point of view of application because of their high R_s. However, the parameters which determine the electrical resistance of these composite materials are numerous and their effects may combine in a complex way. Evidence for one of these factors, the structure swelling (prior to measuring electrical resistivity or testing in electolysis) is discussed below.

In the water electrolysis tests the VP–DVB–asbestos composite material was used as gasket ring in the gas collecting tubes and as separator of the anodic and cathodic compartments of microcells[19] using 40–50% w/w KOH at atmospheric pressure between 90°C and 120°C and at 20–35 bars and 165°C. The results (*Table 3*) show that the material weight loss in the microcell experimental conditions, is five times greater than that (*Table 2*) observed in the static exposure tests. In the microcell experiments the average weight loss of the gaskets was 50% w/w (similar to that of the separators). Under comparable experimental conditions (KOH % T and P) however the weight loss rate of the separators was three times that of the gaskets.

The i.r. spectra of the specimen tested under electrolysis do not differ significantly from those of the samples tested under static conditions. The chemical structures of the inorganic and organic components (which are left on the cardboard) and the VP–DVB/asbestos weight ratio do not appear to be altered on changing the ageing experimental conditions; from those of the simple exposure to the chemical action of the alkali, to the more severe ones in the microcell experiments. Morphologically, however, and more coherently with the weight loss data, the structure void fraction appeared higher in the microcell samples (*Figure 10*) than in the samples recovered from the static tests (*Figure 8b*). The former structure is less compact; several holes appear in it as a result of material erosion.

On cross-checking the weight loss, i.r. and *SEM* data, it appears that the higher weight loss observed during electrolysis is the result of higher mechanical stress rather than the effect of electrically assisted chemical attack by the alkali or electrolytic gases. However, this phenomenon barely affects the cardboard dimensional stability. Gasket rings which have been used (3200 h test) are shown together with a fresh gasket in *Figure 1*. A separator subjected for 1200 h to electrolysis in 50% KOH is shown

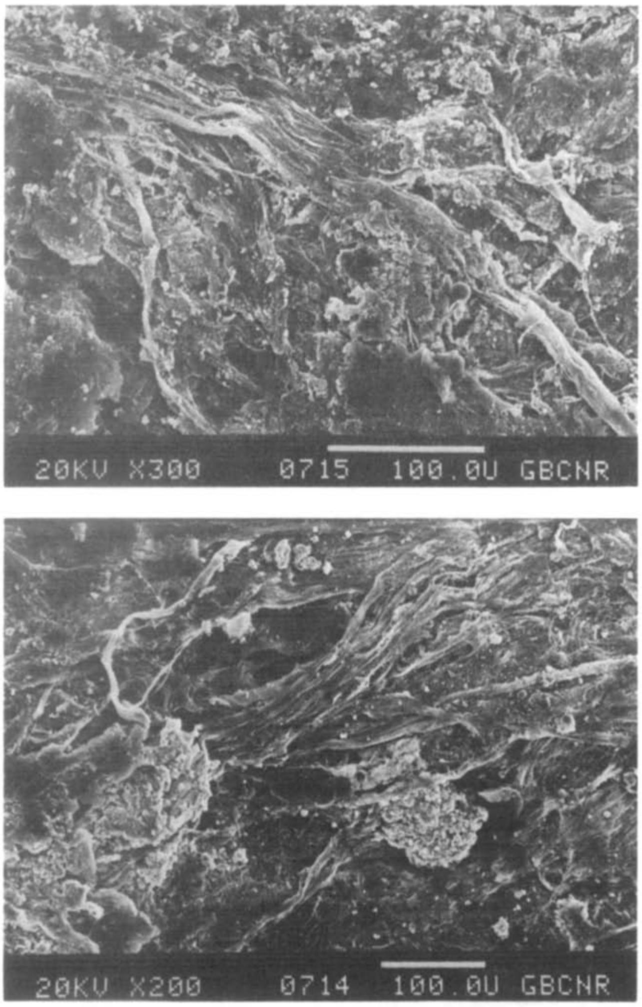

Figure 10 Surface SEM micrographs of VP–DVB (11% w/w)–asbestos cardboard at the end of run b of *Table 3*

together with a fresh one in *Figure 12*.

In terms of separator electrical resistance the high weight loss seems rewarding. Contrary to the case of statically aged samples, the electrical resistance of the microcell separator is greatly affected by the duration of the experiment (*Figure 13*). *Figure 13* also shows an additional effect played by the specimen pretreatment with ethanol. This implies that multiple factors may combine to determine the electrical behaviour of the VP–DVB–asbestos composites. The morphology of the VP–DVB copolymer itself is well known[10–12,15,16], and here has been found to depend on the experimental conditions of the synthesis. The copolymerization of the monomers in the presence of diluents has been reported to yield macroporous materials with higher mechanical flexibility[20], swelling[15] and anion exchange capacity[16,21] and kinetics[20] than the bulk copolymerization does. We ourselves have observed (see Experimental) a macroscopic change from a hard compact, to a soft swollen material (on passing from bulk to suspension copolymerization carried out in the presence of acetone or toluene at any VP/DVB initial mole ratio). This morphological difference is well supported by weight swelling measurements. In the case of *in situ* copolymerized polystyrene–divinylbenzene into asbestos[9] we have shown that the porosity of the organic constituent of the cardboard, and therefore that of the whole cardboard, is enhanced by soaking the material in ethanol as well as in toluene, but not in water. The effect is ascribed to the solvation and subsequent uncoiling effects which ethanol and toluene exert on the organic polymer entangled internuclear chains. Indeed, in the present case of VP–DVB–asbestos

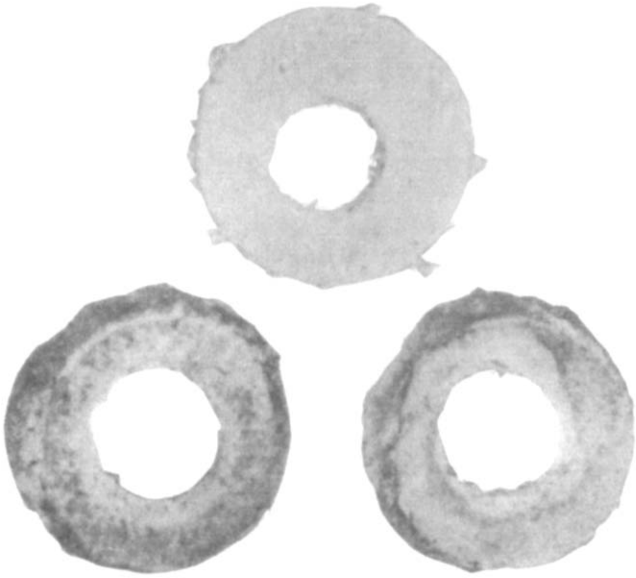

Figure 11 Photograph of VP–DVB (11% w/w)–asbestos gasket rings after 3200 h ageing (sample from run a of *Table 3*): fresh (upper one), aged (lower ones)

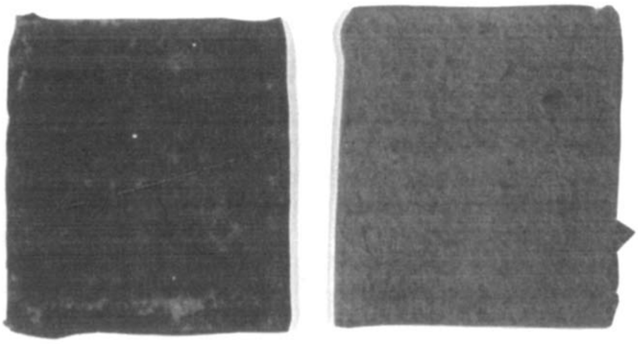

Figure 12 Photograph of VP–DVB (11% w/w)–asbestos separator after 1200 h electrolysis (run b, *Table 3*): fresh (right), aged (left)

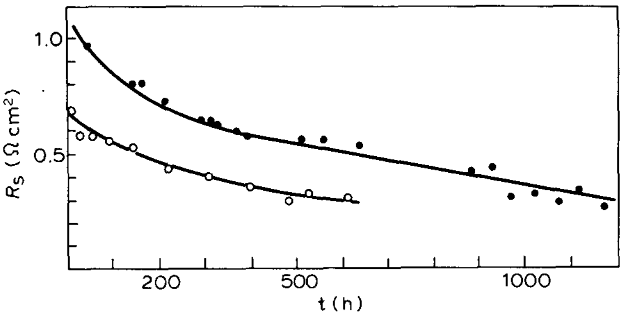

Figure 13 Voltage drop across the VP–DVB (11% w/w)–asbestos separator (sample from run b of *Table 3*) as a function of the time of electrolysis of 50% w/w KOH (aq.) at 90°C and 1 A/cm²: (●) untreated sample and (○) sample presoaked 1 h in EtOH and 1/2 h in 1:2 50% KOH aq.-EtOH at room temperature and 3 h in 50% KOH aq. at 80°C

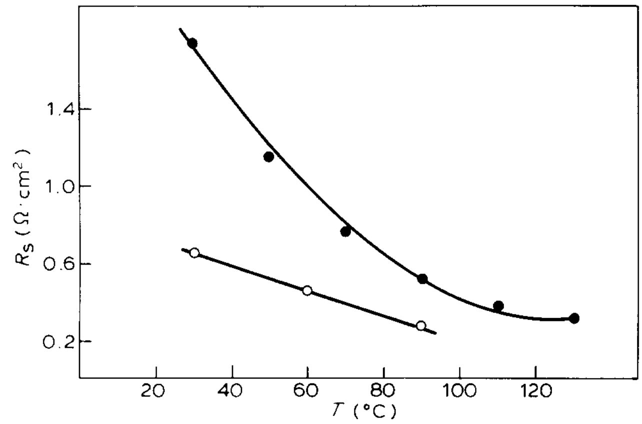

Figure 14 Dependence of the electrical resistance (R_s, Ω cm²) on temperature (*T*, °C) for VP–DVB (11% w/w)–asbestos diaphragm (sample from run b of *Table 3*): (●) and (○) as in *Figure 13*

materials, the effect of pretreating the cardboard with ethanol and alcoholic KOH is striking (see *Figure 13*); the preswollen material shows (at a current density of 1 A/cm² and at 90°C in 50% KOH) an initial potential drop of 660 mV, whereas the untreated material has an electrical resistance of over 1 Ω cm². The R_s difference (above) is even higher at lower temperatures (*Figure 14*). In the non-preswollen material the temperature effect on the structure swelling is evidently higher. *Table 4* reports the data obtained for two different 25 cm² samples taken out of the same VP–DVB loaded 100 cm² specimen which had been previously exposed for 600 h at 120°C to 36% w/w KOH chemical action only. It may be observed that the R_s values for the untreated material are enormously different, whereas those of the preswollen material differ only by 0.01–0.12 Ω cm². It seems that the degree of chain entanglement in the VP–DVB polymer and, therefore, its macroporosity vary quite randomly throughout the cardboard, but the final state or the morphological uniformity which is achieved by solvent swelling is more uniform. The ethanol effect, *vice versa*, is not observed on the plain asbestos material.

In addition to the morphology of the organic copolymer other effects on the electrical resistance of the cardboards are induced by the material weight loss and, partly, by the previously discussed change of the inorganic constituent chemical structure caused by the limited chemical attack by the alkali. The dependence of the ohmic drop on the electrolysis time (*Figure 13*) is certainly due for the major part to the material weight loss and the overall porosity increase. A limited hydrolysis of asbestos may also contribute to make the material more hydrophilous and, therefore, more conductive.

CONCLUSION

The *in situ* copolymerization of vinylpyridine and divinylbenzene within 0.055 cm thick crysotile asbestos cardboards leads to the growth of crosslinked polyvinylpyridine–divinylbenzene on the asbestos fibres and provides an easy mean of protecting asbestos uniformly from the chemical attack of hot concentrated alkalis. Thus composites of higher mechanical strength but lower wettability are obtained on increasing the VP–DVB load into the material. The reinforced asbestos cardboards appear suitable for a variety of industrial applications where the plain cardboard fails due to the limited mechanical and chemical stability of asbestos in hot concentrated alkalis.

Since most of these applications are electrochemical (e.g. batteries or brine and advanced alkaline water electrolysers), the electrical resistance of the VP–DVB–asbestos composites has equal importance as chemical stability and mechanical strength. At least three factors have been recognized to determine the electrical behaviour of these materials when used as separators into the electrolyte: (i) the morphology of the *in situ* VP–DVB copolymer obtained, (ii) the overall porosity and (iii) the HLB of the composite. With respect to the first factor alternative synthetic procedures (i.e. carrying out the *in situ* polymerization of the sorbed monomers into asbestos in the presence of a high boiling solvent) may yield a more macroporous VP–DVB copolymer and, thus, more conductive composites. As to the other factors, both a consistent weight loss as that caused by high mechanical stress during performance in advanced alkaline water microelectrolysers and, to a minor extent, the limited hydrolysis of the asbestos matrix improve the electrical resistivity of the separator.

During electrolysis at 90°C–120°C in 50% KOH the VP–DVB–asbestos material is stable for more than 1000 h as could be demonstrated for a series of 12 diaphragms. It must be mentioned that two samples of the 4–VP–DVB reinforced asbestos diaphragm failed in their function after 580 and 650 h being nearly completely disintegrated. In these experiments the working temperature exceeded 100°C and reached 120°C–130°C during no more than 30 h for electrode activation testing demand. The rest of a deteriorated diaphragm is shown in *Figure 15*. A similar aspect had a diaphragm which was tested at Marcoussis Laboratories[22] at 30 bars, 125°C and 1 A/cm² in 40%

Table 4 Dependence of the electrical resistance (R_s) of VP–DVB (11%w/w)–asbestos and plain asbestos cardboards on ethanol preswelling

Sample	*T* (°C)	R_s (Ω . cm²)[a] untreated[b]	R_s (Ω . cm²)[a] pretreated[c]	ΔR_s (Ω . cm²)[d]
VP–DVB–asbestos[e]				
(e)	30	3.35	0.61	2.74
	50	2.34	0.57	1.77
	65	1.58	0.39	1.19
	80	1.16	0.35	0.81
	100	0.64	0.28	0.36
(ee)	30	8.73	0.73	8.00
	50	7.82	0.49	7.33
	65	6.35	0.43	5.92
	80	5.17	0.37	4.80
	100	3.67	0.27	3.40
plain asbestos	30	0.18	0.20	−0.02
	50	0.14	0.12	0.02
	65	0.12	0.13	−0.01
	80	0.10	0.10	0.00
	100	0.08	0.09	0.01

[a] Measured in 30%w/w KOH

[b] Measured after washing with H_2O to neutral pH and drying at 120°C for 24 h

[c] Treated as above, then soaked in a 1:1 mixture of EtOH and 30% KOH (aq.) and mounted wet in the measuring cell

[d] $\Delta R_s = R_s$ (untreated) − R_s (pretreated)

[e] (e) and (ee): two different 5 cm² samples taken from a 100 cm² specimen

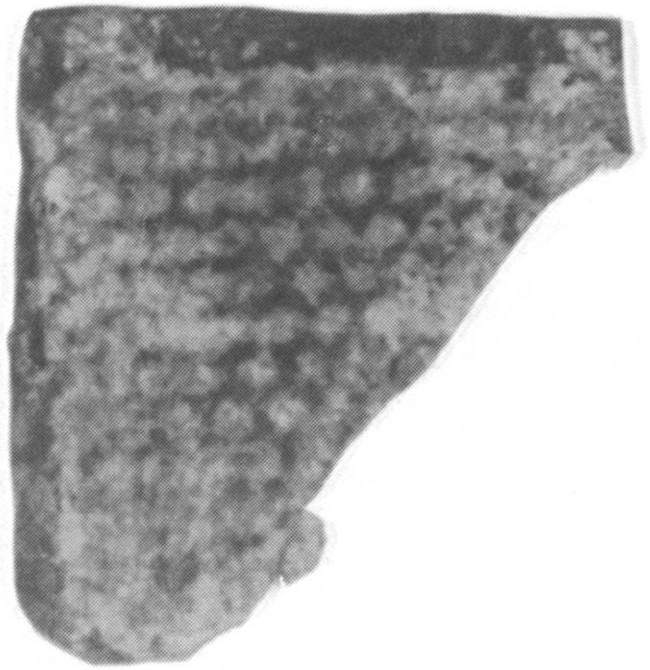

Figure 15 Rest of a deteriorated VP–DVB (11% w/w)–asbestos diaphragm

KOH. In this case the operating cell voltage was found to increase in contrast with the previously mentioned results on the decrease of the separator R_s with the electrolysis time. The exact nature of these accidents has not been established yet. These facts certainly point out that the transfer of laboratory data obtained in pilot equipment to industrial electrolysers may require, as it is often the case, a good deal of additional development and optimization work at all levels (materials and equipment).

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