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Effect of chlorosulfonation of ultra-high strength polyethylene fibres on mechanical properties and bonding with gypsum plaster

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SUMMARY

Ultra-high strength polyethylene fibres were chlorosulfonated according to Kanig's technique. It has been found that the tensile strength of the fibre decreases during chlorosulfonation, whereas the Young's modulus can be increased by more than fifty percent of its original value. The interfacial bond-strength between polyethylene and gypsum plaster could be improved at least 4.8 times, amounting values of 6.3 MPa, making these fibres very suitable for use as a reinforcing material in gypsum plaster. SEM indicated that this improvement could be described to surface roughening of the fibre, due to chemical degradative stress-cracking during constrained chlorosulfonation.

INTRODUCTION

Ultra-strong polyethylene fibres, produced by the gel-spinning/hot-drawing technique (1-4) may be very well suited for reinforcing cement and gypsum. Studies by Hannant and Zonsveld (5, 6) showed that polymeric fibres could easily replace asbestos, if they have a high tensile-strength and Young's modulus as well as a good interfacial bond-strength with the inorganic matrix (7).

The chemical constitution and roughness of the polymeric surface are of great importance in achieving an appropriate interfacial bond between matrix and fibre (8). Several etching techniques have been developed to change the morphology and the chemical properties of polymeric surfaces (9-11).

The purpose of the present study was to explore whether chlorosulfonation of polyethylene fibres, a technique developed by Kanig (12), might provide sufficient bonding to matrices such as cement and gypsum plaster. We have therefore investigated the influence of chlorosulfonation of polyethylene fibres on the interfacial bond-strength between the fibre and gypsum plaster and on the mechanical properties of the fibre.

It will be shown that the interfacial bond-strength between the polyethylene fibre and gypsum plaster can be improved at least 4.8 times by the chlorosulfonation technique. During chlorosulfonation the tensile strength of the fibre decreases whereas the Young's modulus can increase more than fifty percent of its original value.

EXPERIMENTAL

The filaments used in the present work were prepared according to the gel-spinning/hot-drawing technique described elsewhere (13). Non of the fibres was drawn to the maximum draw ratio. The constrained treated

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fibres were loosely wound around a small glass tube, to prevent damaging of the fibre and were subsequently immersed in pure chlorosulfonic acid. After treatment the fibres were thoroughly washed with sulfonic acid, water/sulfonic acid 50:50, demi-water and aceton. The fibres were dried to constant weight in vacuo.

The preparation of the samples used for determining interfacial bond-strength is described in great detail elsewhere (14). The mechanical properties of the fibres were determined with a Zwick Z1.3B tensile tester at a cross-head speed of 12 $mm.min^{-1}$ and an original sample length of 25 mm. For each filament the tensile strength at break and Young's modulus were determined as the average of at least six measurements.

Scanning electron microscopy (SEM) micrographs were taken using an ISI-DS 130 microscope operating at 40 kV, from cold-covered samples.

RESULTS AND DISCUSSION

Figure 1 shows the influence of constrained chlorosulfonation at 80°C of a ultra-high molecular weight polyethylene (UHMWPE) fibre (filament A_2) on the tensile strength at break σ_b and the Young's modulus. This influence of chlorosulfonation on the mechanical properties is depending on the morphology of the fibre starting with and on the chlorosulfonation conditions as reaction temperature and the way of treatment (unconstrained - or constrained treatment). All the fibres investigated showed the same mechanical characteristics. The tensile strength decreases during chlorosulfonation and the Young's modulus first increases to a maximum of more than fifty percent of its original value and than decreases. For this

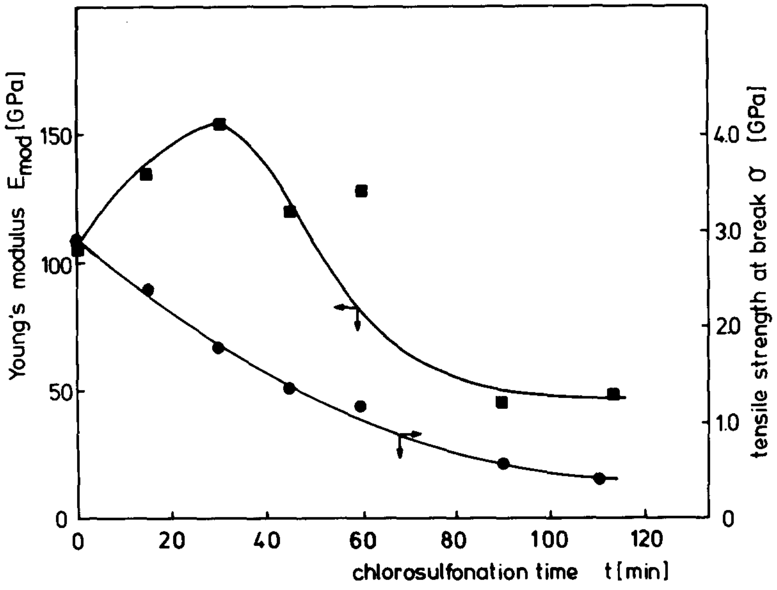

Figure 1 Young's modulus and tensile strength at break as a function of constrained chlorosulfonation time at 80°C for filament A_2

filament A$_2$ the Young's modulus reached a maximum of 155 GPa after 30 minutes of constrained chlorosulfonation at 80°C. Chain modification (12) and cross-linking (15, 16) in the amorphous domains without destruction of the crystal domains might be responsible for this increase in Young's modulus. In the period in which the Young's modulus increases the length of the fibre is almost constant. After 30 minutes the fibre is saturated with chlorosulfonic acid and the acid begins to react on the surface layers of the fibrils. Repulsion of electronegative groups ($-SO_3^-$, $-OSO_3^-$) at the fibril boundaries as well as stresses induced from reaction in amorphous domains (17) and retraction (18) leads to swelling of the fibrils. Because of this swelling the fibrous material becomes accessible for the chlorosulfonic acid and the fibrils distort leading to a decrease in Young's modulus. During this period the fibre shrinks more than fifty percent. This enormous shrinkage can be described to the weakening of the fibrils, resulting in relaxation of the extended chains to their random orientation, releaving the internal or residual and surface stresses. Shrinkage of the fibre may also be brought about by a trans-to-gauche conformation change during chlorosulfonation (17). These changes lead to a build up of internal stresses sufficiently large to distort the lattice in crystallites adjacent to chlorosulfonated regions or induce swelling of the crystallites.

Figure 2 illustrates that although the tensile strength of an UHMWPE fibre (filament A$_1$) decreases during chlorosulfonation the bonding between the polyethylene fibre and gypsum plaster can be improved at least 4.8 times. For the UHMWPE fibre in gypsum plaster the shear traction (19,20)

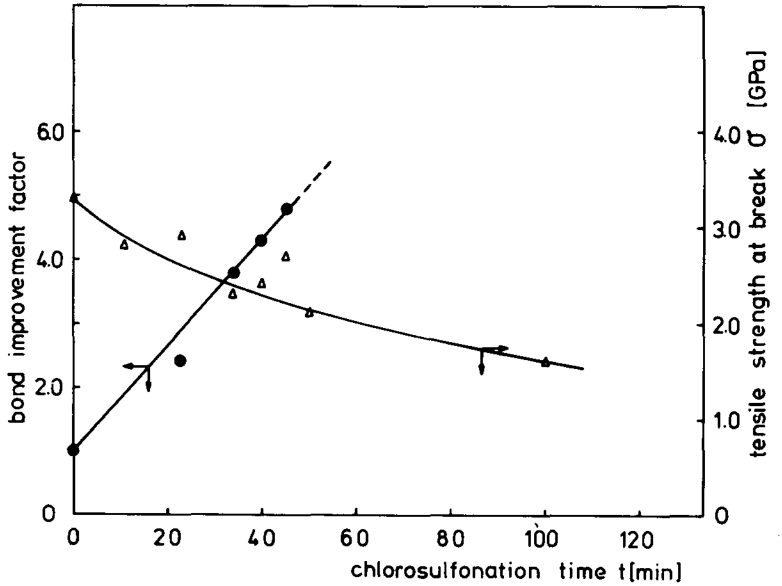

Figure 2 Bond improvement factor (B.I.F.) and tensile strength at break as a function of constrained treatment time with chlorosulfonic acid at 60°C for filament A$_1$.

τ_b is 1,3 MPa and for cases where fibre failure occures τ_b has a minimum of at least 6,3 MPa. These values are comparable to those obtained by de Vekey (20) for glass reinforced concrete and higher than those for asbestos reinforced concrete. For this polyethylene filament the bond improvement factor (B.I.F.), defined as

$$\text{B.I.F.} = \frac{\text{pull out load chlorosulfonated filament}}{\text{pull out load polyethylene filament}},$$

increases and reaches a value of 4.8 after 45 minutes chlorosulfonation at 60°C. This value is not a maximum. After 45 minutes chlorosulfonation the interfacial bond-strength still increases, but the limitation for further improvement is the tensile strength of the fibre itself.

The improvement of the interfacial bond-strength between the polyethylene filament and the gypsum matrix can be attributed to the roughning of the polymeric surface during the chlorosulfonation reaction. In a previous investigation to the fracture process of UHMWPE fibres (18) was shown that the fibres were preferential attacked at surface irregularities, such as kink- and shear bands, if they were exposed to chlorosulfonic acid. These shear bands occur at regular distances (100-500 µm) along the fibre and might be formed by vibration of the drawing-motors, causing compressive forces in the fibre during hot-drawing and a telescopic sliding of the outer layers over the fibre core which lags behind in temperature. Figure 3 illustrates a UHMWPE fibre after 120 minutes constrained chlorosulfonation at 80°C. The fibres start to degrade in the direct vicinity of shear-bands. Cracks occur at regular distances on the fibre surface.

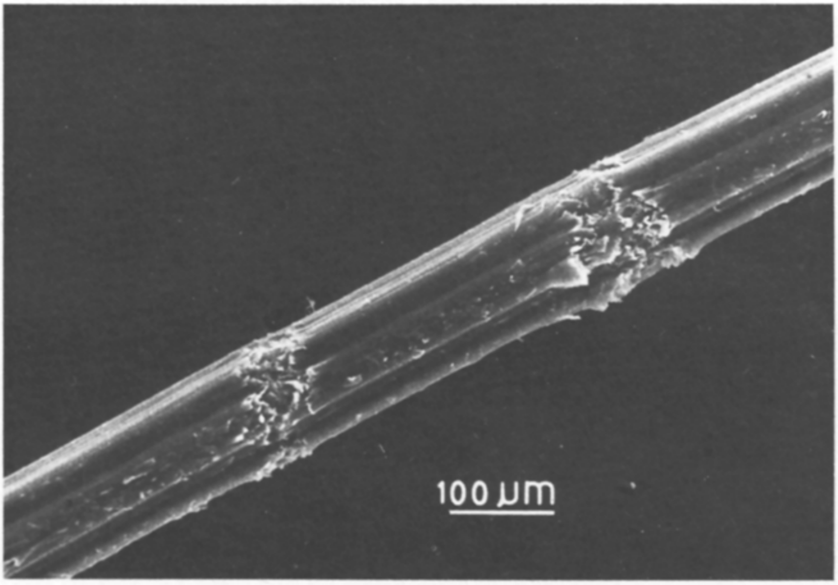

Figure 3 SEM of an UHMWPE fibre after 120 minutes constrained chlorosulfonation at 80°C showing spots where chemical stress-cracking is initiated.

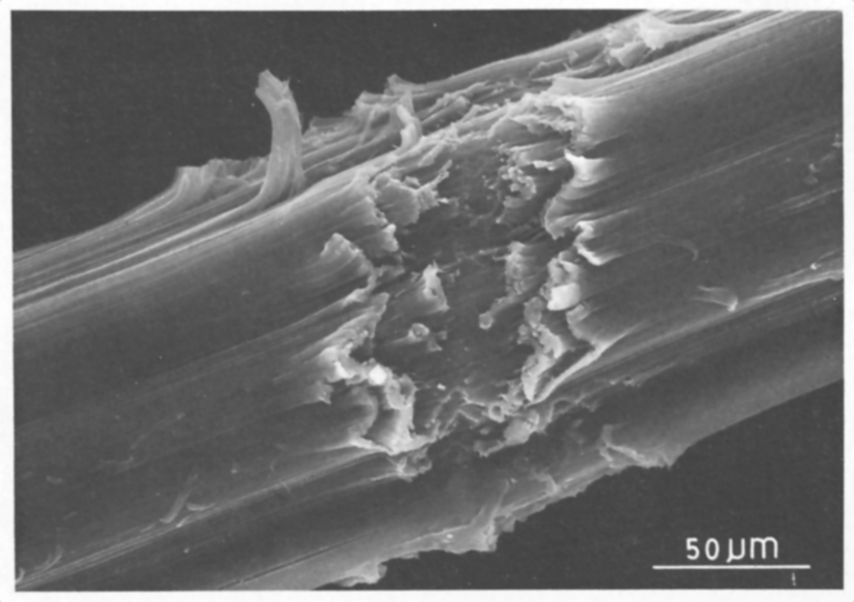

Figure 4 SEM of an UHMWPE fibre after 120 minutes constrained chlorosulfonation at 80°C showing the layered structure.

Figure 4 illustrates that fibrils were broken all around the fibre leading to circumferential cracks, which penetrate in straight line perpendicular to the fibre axis, from the surface to the interior of the fibre. This cracking is accompanied by chain-rupture, giving rise to lowering the mechanical properties of the fibre.

The cracking behavior of the constrained chlorosulfonated polyethylene filaments can be explained by chemical degradative stress-cracking. Shanahan (21) showed that a given liquid is always capable of giving rise to environmental stress-cracking if the applied stress is in the order of 10 MPa. Smook (22) showed that the retractive stress of a constrained UHMWPE fibre at 60-80°C is also in this order of 10 MPa. This retractive force can have a synergistic effect on the chemical degradative cracking of polyethylene filaments during chlorosulfonation at 80°C. Due to this cracking process the filaments get an enormously rough surface, which is strictly necessary for an improved bonding between polyethylene fibres and gypsum plaster.

As already shown in figure 1 little cracks and flaws in the surface of the UHMWPE fibre didn't, in contrast with a lot of other fibres, extensively affect the mechanical properties of the fibre. Only after prolonged treatment, the tensile strength and Young's modulus decreased to values lower than 1 GPa and 50 GPa, respectively.

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