JOURNAL OF MATERIALS SCIENCE 28 (1993) 5002–5006

Treated polyethylene fibres as reinforcement for epoxy resins

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Ultra-high-modulus polyethylene (UHMPE) fibres were treated in order to develop favourable surface and, possibly, microstructure characteristics. The main aim was to eliminate the microfibrillar morphology of the fibre and improve interfacial bonding between fibre/matrix so that better compressive properties can be achieved in reinforced resins. Calendering at 130 °C was performed, and the surface treatment used oxidative solutions. Adhesive bonding to epoxy matrices was highly improved in chromosulphate-treated material exceeding that of a commercial, corona-treated product, but the mechanical properties of these fibres deteriorated. Calendering did not significantly affect fibre strength and only improved adhesive bonding slightly. The use of these treated reinforcements is expected to improve the performance of composite materials, especially at low fibre volume fractions, because of their improved interfacial characteristics.

1. Introduction

The incorporation of particulate fillers, short and continuous fibres or even fabrics into polymeric materials is a popular technique aiming at increasing the modulus and strength of the final product, provided that the reinforcement is intrinsically much stiffer and stronger than the base polymer. This is especially critical in case of thermosets, such as epoxies, which are very brittle materials despite their excellent physico-mechanical properties.

The prediction of the properties of composites, based on the characteristics of the matrix and the reinforcing element, has attracted the interest of researchers for a long time. It is generally assumed that each constituent of the composite behaves as it would in isolation, which means that interactions are not taken into consideration. Various theories have been proposed and the approach is sometimes different, but the approach which is mostly used is based on the *Law of Mixtures*, which predicts the longitudinal and transverse response of a simple composite specimen, with fibres oriented parallel to their axes, by assuming respectively a parallel and a series reaction to the applied load [1]. Many studies have already been published on the use of various fillers. The reinforcing effect of carbon fibres on the mechanical properties of acrylic matrices has been reported [2, 3] along with other fillers such as carbon black [4], aramid fibres or combinations of glass and carbon fibres for the production of hybrid composites [5]. Some work has also been made on the use of common fibres as reinforcements [6] whereas other authors deal with mechanical behaviour and fibre–matrix interactions [7–9].

Among the new, advanced-technology reinforcements, ultra-high-modulus polyethylene (UHMPE) fibres are of profound interest. They have been tested as a reinforcement and an improvement in impact strength in acrylic resins was found [10, 11], but the flexural strength and modulus seemed not to improve [12, 13].

The unique properties of UHMPE fibres are due to their fully extended and aligned chain configuration. There are several methods available for the production of these fibres, based on the deformation of a gel or a solid. Thus, Smith and Lemstra proposed the technique of ultradrawing polyethylene fibres crystallized from solution [14], whereas Zwijenburg and Pennings developed the surface-growth method, i.e. the drawing of a wet gel of ultra-high-molecular-weight polyethylene, with concurrent crystallization [15–18]. The mechanical properties obtained by this latter process can be further improved by special drawing procedures, such as hot drawing [19, 20], zone drawing or zone annealing [21, 22]. In addition to the above methods, the possibility of achieving high modulus/high strength polyethylene by melt extrusion has been studied [23–25], and successful results have been reported by Bashir and Keller [26].

However, a recognized weakness of UHMPE fibres is their low strength in directions perpendicular to their axis, i.e. perpendicular to the drawing/orientation direction. This leads to highly anisotropic products when composites are produced and gives poor performance characteristics in cases of complex loading. This anisotropy in strength is due to the fibre morphology, which is a result of the production process. In fact, the morphology of UHMPE is microfibrillar, consisting of smooth or "shish-kebab" fibrils [27]. More specifically, a shish-kebab morphology is composed of core microfibrils with nearly extended

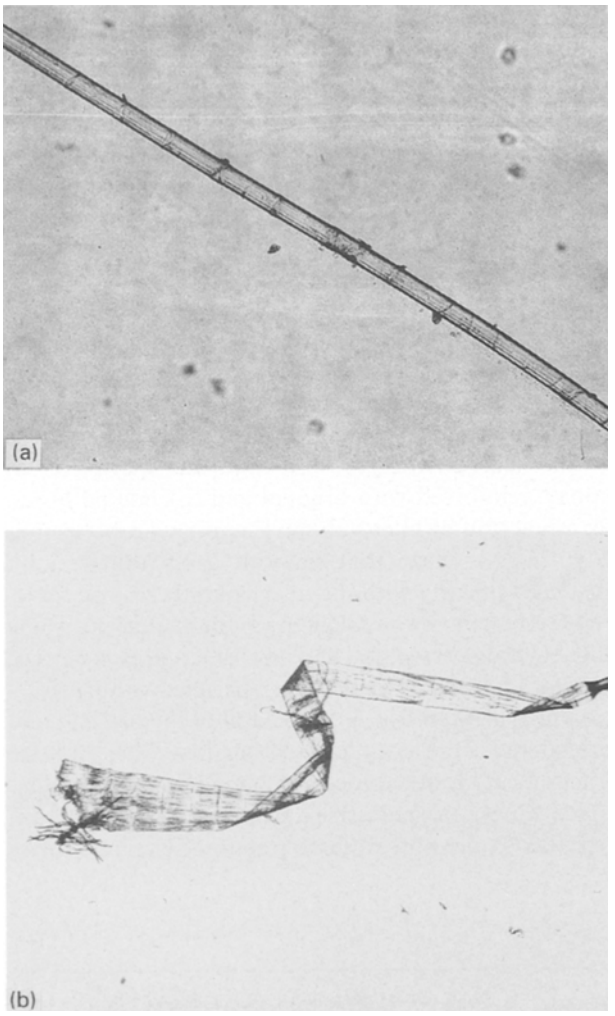

Figure 1 (a) Original UHMPE fibre, and (b) calendered UHMPE fibre.

chains and a number of folded-chain platelets attached to the cores [28–31]. On the other hand, a smooth fibre contains microfibrils with nearly extended molecules and a negligible amount of lamellar platelets [32, 33].

It should be noted that the poor interfacial properties between fibres and polymeric matrices, due to the non-polar and inert character of polyethylene, further enhances the effect of anisotropy on mechanical strength. Many studies have been published on the mechanical properties of UHMPE fibres [34–36] and several surface treatments have been proposed to promote adhesion to polymeric matrices [37–39], including coating, etching and chemical modification of the surface of the fibre.

In this work an attempt was made to optimize the performance of UHMPE fibres in epoxy-matrix composites, focusing on both fibre-surface treatment to promote interfacial bonding with the epoxy matrix and modification to alter the shape and microstructure.

2. Experimental procedure

A commercial UHMPE fibre was used in this work, namely, Tekmilon NA 310 (Mitsui Petrochemicals Industries Ltd., Japan). Corona-treated fibres were also used for comparison. The epoxy resin used was a two-component system based on diglycidyl ether of Bisphenol A and an oligomeric amide as hardener (Epikote 828 and Epilink 175, Shell Chemicals Hellas).

Chromosulphate and permanganate solutions were used as oxidative agents for surface treatment of the fibres. The consistency of the chromosulphate solutions was: 7 g $K_2Cr_2O_7$, 150 g H_2SO_4 (98%), and 12 g H_2O. The permanganate solution was a mixture of 98% H_2SO_4 and 85% H_3PO_4 (2:1 per volume) containing 1% per weight $KMnO_4$. Also, surface etching of the fibres was attempted by the use of a mixture of solvents (toluene/*n*-propanol, 30/70 per volume). The fibres were immersed in the solutions for varying periods and treated at temperatures up to 120 °C.

Another treatment was calendering at a temperature of 130 °C in a two-roll mill (Scamia, France). The effect on shape of calendering was observed in an Amplival optical microscope (Jenoptik Jena GmbH) equipped with a camera to record microscopic images. The same instrument was used to determine the contact angle of liquid epoxy and unsaturated polyester resin on the treated UHMPE fibres, since it is a measure of the interfacial surface tension indicating the wettability. Suitable software, developed by Wagner [40], was used for calculations.

The tensile properties of treated fibres were determined according to ASTM D 3379/75, in an Alphatens V2.1 (England) tensile-testing machine, in order to establish the effect of treatment on the deterioration of strength. The same machine was used for pull-out tests of monofilaments from epoxy, which were performed as an additional means of controlling the adhesive bonding and its dependence on each specific treatment. Furthermore, composite specimens were prepared using epoxy matrices and fibres at various volume fractions. Curing was carried out at 80 °C. Similarly, the tensile properties of those specimens were measured using an Instron TT-CM (England) tensometer.

3. Results and discussion

The contact angle measured in commercial and treated fibres, using epoxy and unsaturated polyester resins, are shown in Table I. From the results, polyester gives much lower angle values, which means that better wetting of polyethylene occurs. However, treatment with chromosulphate appears to have no considerable effect, in most cases, on the contact angle of the system, polyester – UHMPE. On the other hand, the applied treatments seemed to increase wettability of the fibres with epoxy resin, with a minimum in the contact angle corresponding to immersion in chromosulphate at 110 °C for 60 min. The characteristics of corona-treated fibres, a type of UHMPE fibres especially developed for better adhesion to polymeric matrices, were also measured. Wetting, in terms of contact angle, seems to be similar to that of untreated fibres. Since corona attack is a treatment which can produce surface oxidation and/or etching, the same wettability probably means that better adhesion is

achieved by surface roughness rather than oxidation of the fibre.

The tensile properties of chromosulphate treated fibres (90 °C, 60 min) were tested to examine whether a deterioration of mechanical properties accompanies the treatment applied. Similarly, corona-treated fibres, along with the calendered original and calendered corona-treated fibres, were tested for the same reason. The results obtained from the above measurements are shown in Table II.

It can be seen that a modest decrease of about 6% in strength occurs upon calendering of the fibres, but elongation increases considerably, by about 36%. On the other hand, an intense decrease in strength, i.e. approximately 24%, of the corona-treated fibres was recorded after calendering, whereas elongation increased to the same level as the original fibres. This difference in strength decrease between the original and corona-treated fibres might be attributed to further oxidation of the treated fibres at the high temperature of calendering. This interesting fact of an increase in elongation is probably due to some relaxation occurring during calendering in the fully extended polyethylene chains.

The chromosulphate-treated fibres display a sharp decrease in strength, accompanied by low elongation, which suggests that the tensile properties deteriorated. However, this treatment seems to increase considerably the pull-out load up to the level of tensile strength of the fibres. This value is well above the load corresponding to the original fibres and even higher than that of the corona-treated product. Very interestingly, the calendered fibres showed an improved response in the pull-out tests, displaying an increase in load of about 30% compared to the original fibres. These results indicate that the change in shape (Fig. 1) also plays a part in the interfacial adhesion between fibre and matrix. In the case of calendered fibres the shape is transformed from a cylinder to a ribbon, which is likely to have better adherence because of its increased surface area.

The tensile strength of composite specimens of epoxy, reinforced with original and calendered fibres, as a function of filler volume fraction, can be seen in Fig. 2. It is clear that in both cases the strength increases linearly with the filler volume fraction. Also, reinforcement with calendered fibres led to some higher strength values and the differences from the untreated product increase as the filler volume fraction increases. In Fig. 3 the moduli of the original and calendered fibres are plotted against filler volume fraction, and lower values were recorded for the calendered fibre-reinforced specimens, with increasing differences as the fibre volume fraction increases. These

TABLE I Contact angle of various UHMPE fibre samples

Sample	Treatment conditions		Contact angle, θ (deg.)	
	Time (min)	Temperature (°C)	Epoxy	Polyester
Original fibre			40.18	13.02
Corona treated			38.2	–
Chromosulphate treated	60	45	31.83	11.12
	20	60	27.98	10.48
	60	60	37.41	14.16
	60	70	31.26	10.0
	120	70	34.25	13.88
	60	80	40.12	5.78
	120	80	30.32	13.31
	60	90	25.59	14.23
	60	110	25.45	22.51
Permanganate treated	60	90	43.27	–
	60	60	28.56	–
Solvent treated	60	80	28.78	–
	80	70	30.30	–

TABLE II Tensile and pull-out characteristics of treated UHMPE

Sample	Tensile load (N)		Elongation (%)		Pull-out load (N)	
	M[a]	SD[b]	M[a]	SD[b]	M[a]	SD[b]
Original fibre	2.986	0.350	5.759	0.729	0.459	0.147
Calendered	2.810	0.226	7.822	0.667	0.691	0.338
Corona treated	2.823	0.153	5.745	1.449	0.834	0.442
Calendered corona treated	2.130	0.368	7.608	1.890	0.929	0.277
Chromosulphate treated	0.928	0.285	1.200	0.402	0.946	0.311

[a] M: mean value out of ten specimens.
[b] SD: standard deviation.

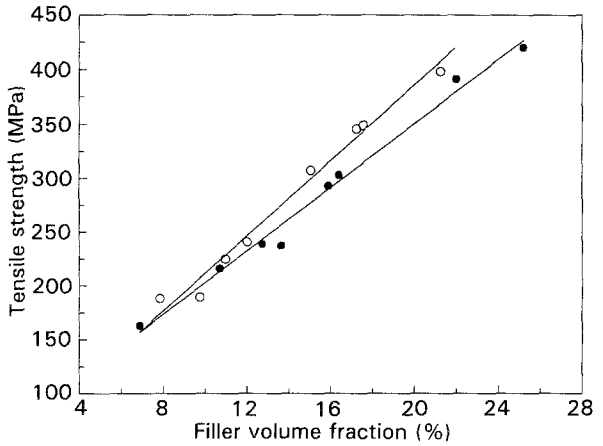

Figure 2 Tensile strength of specimens reinforced with UHMPE fibres: (○) calendered fibre, and (●) original fibre.

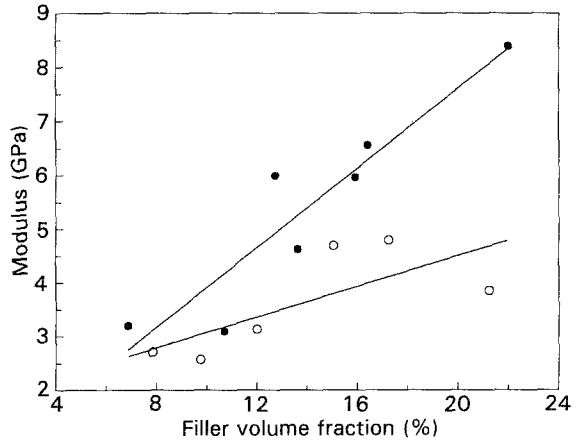

Figure 3 The modulus of elasticity of composite specimens as a function of filler volume fraction: (●) original fibre, and (○) calendered fibre.

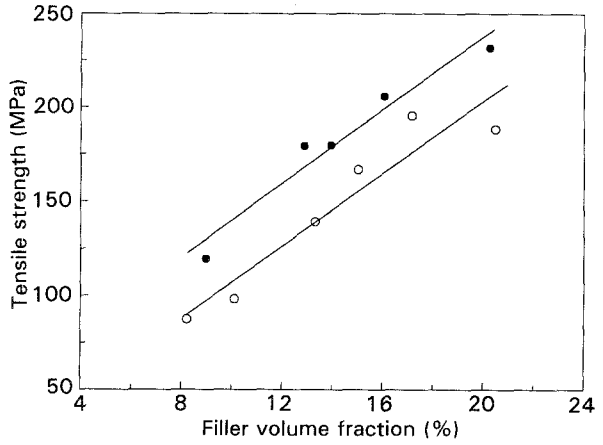

Figure 4 Tensile strength of specimens reinforced with treated UHMPE fibres: (●) corona-treated fibre, and (○) calendered, corona-treated fibre.

results are connected with the tensile characteristics of calendered fibres shown in Table II, i.e. the higher pull-out load and higher elongation observed.

The tensile strength of specimens reinforced with corona treated and calendered, corona-treated fibres is shown in Fig. 4. In this case, the strength of specimens reinforced with calendered fibres is lower, but this difference seems to remain constant for filler volume fraction in the range 8–20%. The moduli plotted in Fig. 5 show a similar relationship.

The tensile strength and modulus of epoxy specimens reinforced with untreated and chromosulphate-treated fibres are plotted against filler volume fraction

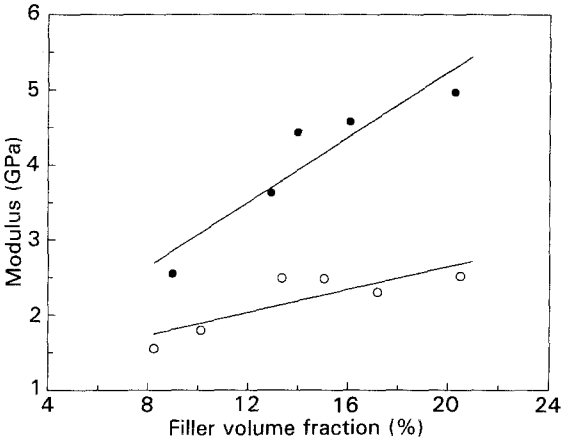

Figure 5 The modulus of elasticity of composite specimens as a function of filler volume fraction: (●) corona-treated fibre, and (○) calendered, corona-treated fibre.

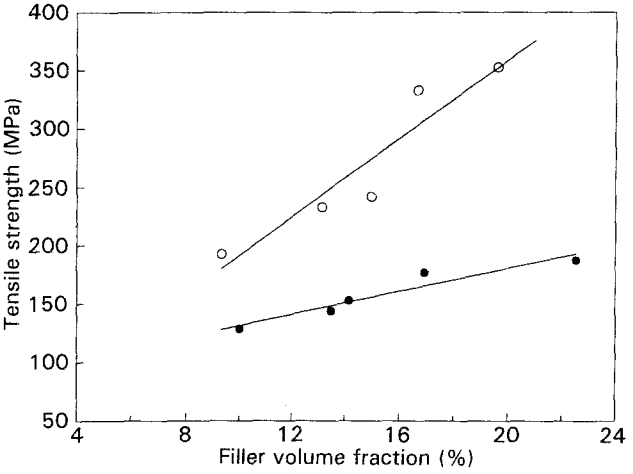

Figure 6 Tensile strength of specimens reinforced with UHMPE fibres: (○) original fibre, and (●) chromosulphate-treated fibre.

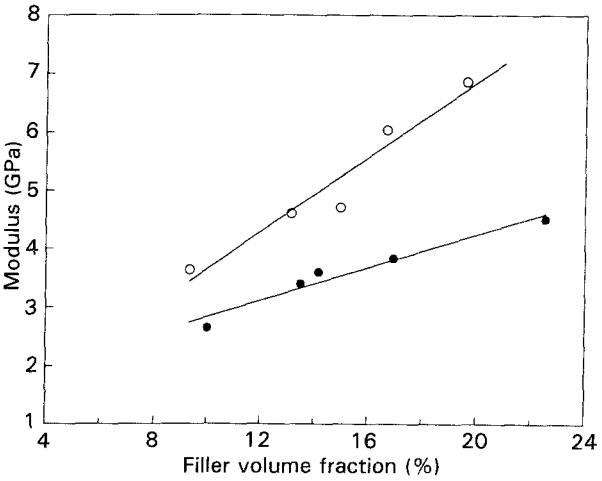

Figure 7 The modulus of elasticity of composite specimens as a function of filler volume fraction: (○) original fibre, and (●) chromosulphate-treated fibre.

in Figs 6 and 7, respectively. It is obvious from these figures that both strength and modulus decrease drastically when chromosulphate-treated fibres are used, especially at higher filler volume fractions. However, even this sharp decrease leads to final products with an acceptable tensile strength. On the other hand, an improvement in other properties might be expected as a result of the promotion of interfacial bonding.

4. Conclusions

1. Calendering of UHMPE fibres, at 130 °C, is a simple, continuous process which improves adhesive bonding of the fibre to epoxy matrices and causes a slight decrease in mechanical strength.

2. Chemical treatment of UHMPE fibres with oxidative solutions strongly enhances adhesive bonding, but it also drastically decreases the fibre strength.

3. Calendered and surface-treated fibres can be used as a modified reinforcement of epoxy resin. A modest decrease in tensile strength and modulus occurs at volume fractions up to 15%, but the improved interfacial characteristics suggest better performance.

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Received 2 October 1992
and accepted 24 February 1993