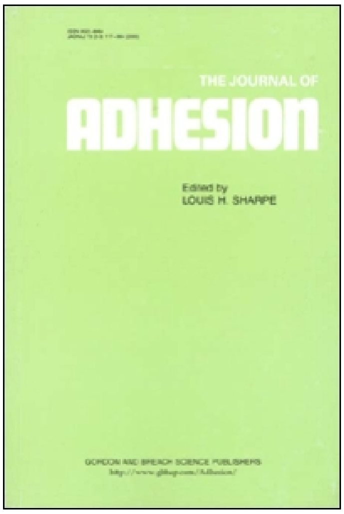

The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

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To cite this Article Tu, L. , Kruger, D. , Wagener, J. B. and Carstens, P. A. B.(1997) 'Wettability of Surface Oxyfluorinated Polypropylene Fibres and Its Effect on Interfacial Bonding with Cementitious Matrix', The Journal of Adhesion, 62: 1, 187 — 211

To link to this Article: DOI: 10.1080/00218469708014569

URL: http://dx.doi.org/10.1080/00218469708014569

J. Adhesion, 1997, Vol. 62, pp. 187–211
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Wettability of Surface Oxyfluorinated Polypropylene Fibres and Its Effect on Interfacial Bonding with Cementitious Matrix

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(Received 28 June 1996; In final form 18 November 1996)

The surface of high molecular weight polypropylene monofilament fibre was modified using a oxyfluorination method. The oxyfluorination treatment level was varied and a hydrolysis post-treatment was also applied. Contact angles of oxyfluorinated, hydrolyzed oxyfluorinated and unmodified polypropylene fibres were obtained by dynamic contact angle (DCA) measurement using three liquids of known dispersion, acid and base surface free energy components. The surface free energies were then calculated according to the acid-base theory developed by Good, van Oss and Chaudhury. Surface oxyfluorination largely increased the acid and base components of the fibres' surface free energy compared with unmodified polypropylene fibres. The oxyfluorinated and unmodified polypropylene fibre surfaces were observed by Scanning Electronic Microscopy and Photoacoustic Infrared Spectroscopy. It was found that the surface oxyfluorination largely increases the roughness of the polypropylene surfaces and the carbonyl group content increases as the treatment level increases. The interfacial shear bond strengths between the cementitious matrix and the polypropylene fibres treated under various conditions were determined by embedded fibre pull-out tests. Results showed that the fibre surface oxyfluorination treatments increase the interfacial bond strengths. The correlations between the shear bond strengths and surface free energy components were established. Results showed that fibre/concrete interfacial bonding was best correlated with the acid component of surface free energy of polypropylene fibres.

Keywords: Oxyfluorination; surface modification; surface free energy; contact angle analysis; acid-base interactions; polypropylene fibres; cementitious composites; fibre/matrix bonding; interfacial interactions; fibre pull-out test; interfacial shear bond strength

INTRODUCTION

For all fibre reinforced composite materials, the interfacial bonding between the fibre and matrix has a key effect on the mechanical performance of the composites. This is mainly because good interfacial bonding can benefit the load transfer between the fibres and matrix which controls the effectiveness of fibres in enhancing the mechanical properties of fibre reinforced composites in elastic and inelastic stage, as well as the fracture behaviour [1]. Strong fibre/matrix interfacial bonding arises from high wetting of the fibres, mechanical interlocking and formation of strong bonds between the fibre and matrix. Since chemical and physical forces contribute to bonding between the fibre and the matrix, in order truly to understand the nature of interfacial interactions, it is necessary to separate and measure the individual forces leading to fibre/matrix bonding [2]. Polypropylene (PP) fibres have been used in concrete for 30 years to increase the impact resistance, plastic and drying shrinkage cracking resistance and failure strain capacity [1, 3]. The bonding between the PP fibre and cementitious matrix is widely accepted as poor because of the low wettability of PP fibres which arises from the hydrophobic surface nature of polypropylene [1, 3, 4, 5]. The chemical structure of polypropylene makes it non-polar and lacking in acid-base interactions (such as hydrogen bonding capacity), due to its extremely low acid and base surface free energy components [6]. Due to this inherent hydrophobic nature of PP fibres, various manufacturing processes have been developed to produce PP fibres with special shapes or profiles to provide mechanical keying or interlocking for enhancing the fibre/matrix interfacial bonding, such as fibrillated, twisted and button-end PP fibres [1, 3]. The shear bond strengths between the fibres and the cementitious matrices, which varies from 0.3 to 1.0 MPa for fibrillated fibres, are still much lower than the tensile strengths of cementitious matrices which range from 3 to 4 MPa [1, 3, 7]. Thus, in order to exploit the reinforcing potential of PP fibres in concrete, further improvement in interfacial bonding is needed. Modification of the PP fibre surface by chemical reactions to introduce chemical bonds seems to be a promising and effective method for further enhancing the interfacial bonding. Various PP fibres with different profiles have been extensively developed worldwide while pure chemical surface modification of PP fibres for use in concrete has not yet been reported. The purpose of this investigation is to develop surface-modified polypropylene fibres with enhanced interfacial bonding for use in concrete. Especially when combined with special fibre profile manufacturing processes, the surface modification method can ensure optimum bonding.

Oxyfluorination of Polypropylene

The reaction between the fluorine and hydrocarbons was first tried in the last century, but numerous difficulties were encountered. This was mainly because the reaction between fluorine and hydrocarbons is so rapid and exothermic that it often leads to fragmentation and combustion if the reaction is not controlled [8,9].

It was initially thought that the fluorination of hydrocarbon polymers would be an alternative process for producing fluorocarbon polymers. In 1954 a process was described to produce fluorinated polymers by reacting polyethylene with elemental fluorine (on its own or diluted with an inert gas) [10]. In this case, the heat of reaction was controlled by using polyethylene in a form with large surface area (*e.g.* powder) or by contacting it with a metal to dissipate the heat. In the beginning of 1970's, the so called La-Mar direct fluorination process was developed by Lagow and Margrave in which the principal feature is initially infinite dilution of fluorine by neutral gas followed by a gradual increase in fluorine concentration [9,11]. Through careful control of different reaction conditions, from partially-fluorinated polymers up to fully-fluorinated polymers (perfluorinated products) can be obtained.

A different approach to polymer fluorination was also pursued where only the surface of the polymer is modified by fluorine, to give enhanced surface properties, while leaving the bulk properties intact. In 1938 a process for controlling the fluorination rate of elastomers by diluting the fluorine with an inert gas was described [12]. The application in this case was the improvement of the chemical resistance of the elastomer, *i.e.* only the surface needed to be modified. Other workers found that fluorination with elemental fluorine (pure or diluted) leads to enhanced printability and reduced gas permeation of polyethylene containers [13,14]. Schonhorn and Hansen fluorinated polyethylene with elemental fluorine (pure and diluted with argon) and found enhanced adhesion with epoxy adhesives [15]. They also determined the surface free energy of the treated polymer and found it to be lower than that of untreated polyethylene. From this they concluded that the enhanced adhesion resulted from the removal of a weak boundary layer and that wettability was not as important for adhesion as previously thought. The modern methods for surface energy determination (see next section) did not exist at the time this work was published, and we know that the method they used was incomplete.

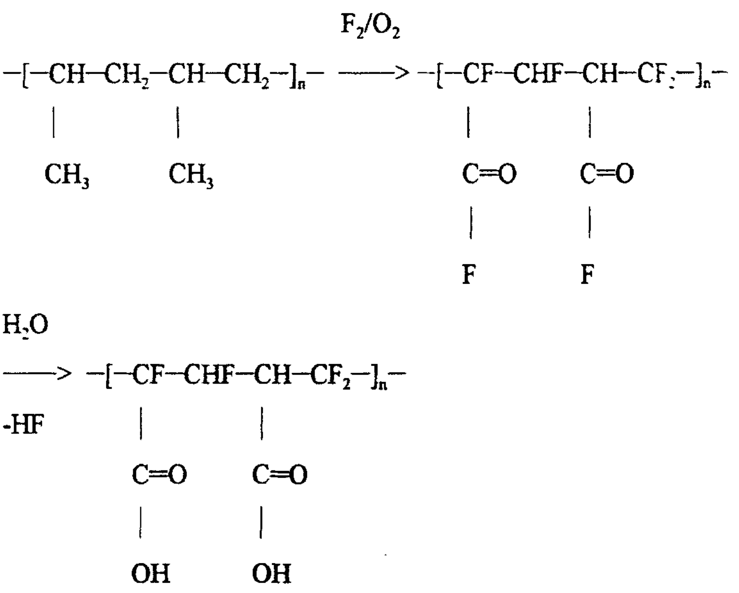
Eschwey *et al.* investigated the effect of fluorination and oxyfluorination on surface topography [16, 17]. They found that in-line fluorination of motor car petrol tanks led to a wrinkled surface, but this was attributed to cooling in the mould rather than because of fluorination. If fluorination was carried out at temperatures lower than the melting point of the polymer, the surface topography remained unchanged. Oxyfluroination under certain conditions (where the oxyfluorination gas mixture contains more O_2 than F_2) led to etching of the surface. This etching produced a very smooth and glossy surface, which not only had an improved appearance, but also good solvent barrier properties.

Brewis *et al.* found that high-density polyethylene (HDPE) and low-density polyethylene (LDPE) gave good adhesion with epoxy adhesives after both fluorination and oxyfluorination [18, 19]. They attributed this to increased polarity of the surface.

Kolpakov *et al.* investigated the mechanism of fluorination and oxyfluorination of polystyrene (PS) and concluded that a free radical process takes place [20].

Kranz *et al.* did a detailed study of fluorination and oxyfluorination of PE and PP [21]. They found increased adhesion with epoxy adhesives with both fluorination and oxyfluorination. This was attributed to a considerable increase in surface energy and polarity. No topography change was observed with SEM, but AFM showed an increase in microroughness, attributed to the different sizes of the H and F atoms.

According to several authors, the oxyfluorination process proceeds with a free radical chain mechanism, with the oxygen inhibiting the reaction rate [20, 22, 23, 24]. When a F_2/O_2 gas mixture is used in fluorination, functionalization of polymers can be achieved as the molecular oxygen spontaneously reacts both with the fluorocarbon and alkyl radicals generated in the fluorination process, resulting in a free radical chain reaction which incorporates oxygen-containing groups (such as the carbonyl group, C=O) into the polymer [8, 23]. Oxidation of the polymer during oxyfluorination preferably occurs at pendant alkyl group sites, such as the methyl group in polypropylene, to produce acid fluorides at these sites. When such acid fluorides are contacted with H_2O in the air or purposely undergo hydrolysis, they are converted to carboxyl groups (—COOH), which is a major process for functionalization of polymer surfaces [9]. In this investigation, the polypropylene fibres were oxyfluorinated using a F_2/O_2 gas mixture at room temperature, followed by a hydrolysis post-treatment. The reaction process can be typically described as follows:



$$-[-\underset{\displaystyle CH_3}{CH}-CH_2-\underset{\displaystyle CH_3}{CH}-CH_2-]_n- \xrightarrow{F_2/O_2} -[-\underset{\underset{\displaystyle F}{C=O}}{CF}-CHF-\underset{\underset{\displaystyle F}{C=O}}{CH}-CF_2-]_n-$$

$$\xrightarrow[-HF]{H_2O} -[-\underset{\underset{\displaystyle OH}{C=O}}{CF}-CHF-\underset{\underset{\displaystyle OH}{C=O}}{CH}-CF_2-]_n-$$

STRUCTURE 1

After introduction of F atoms into polypropylene to partially replace the H atoms on the hydrocarbon molecular chain, the electron cloud of the C—F bond is attracted towards the F atom because of the high electronegativity of fluorine. Therefore, the C atom becomes partially electropositive and attracts the electron cloud of the C—H bond towards itself which makes the H atom become more electropositive.

Because of the above mechanism, the oxyfluorinated polypropylene is much more Lewis acidic than unmodified polypropylene. Due to the polarization of π bonding electrons of carbonyl groups (C=O:), the O-atom becomes partially electronegative and the C-atom partially electropositive [25]. Thus, the carbonyl group C=O: with lone pair electrons and exposed π bonding electrons possesses strong electron donating capacity [26], which greatly increases the Lewis basicity of PP fibres. The polarization of π bonding electrons also increases the dispersion forces of PP fibre surfaces due to the possible increase in induced dipole-dipole interactions. On the other hand, incorporation of C=O groups and F atoms simply increases the polarity of polypropylene which increases the polar component of surface free energy of polypropylene. After hydrolysis, most acid fluoride groups are converted into carboxylic acid groups, —COOH, in which the lone electron pair on the O-atom of the —OH group conjugate with the double bond of the C=O group. Because of this conjugation, the electron cloud of $-COO^-$ is evenly distributed between two O atoms which, on the one hand, makes the H-atom become strong Lewis acidic, but on the other hand, reduce the electron donating capacity of the O-atom on the C=O group [25]. Therefore, hydrolyzed oxyfluorinated polypropylene exhibits not only Lewis acidity, but also reduced basicity due to the decrease in Lewis basicity of the C=O group in —COOH as well as the decrease of pure carbonyl group (R—C=O) content compared with oxyfluorinated polypropylene.

The Acid-Base Interaction Concept

Fowkes *et al.* suggested that the surface free energy, γ, of a condensed phase could be divided into two main components according to the different forces involved in molecular interactions, *i.e.*, γ^d and γ^p, which refers to the dispersive component and the polar component of surface free energy, respectively [27], according to the equation: $\gamma^{\mathrm{Total}} = \gamma^d + \gamma^p$.

This was later refined by Good, Van Oss and Chaudhury [6, 2] by including in the dispersive component arising from all the electromagnetic interactions of molecular pairs, triplets and quadruplets, etc., due to oscillating temporary dipoles, permanent dipoles and induced dipoles interactions (called the Lifshitz-van der Waals component γ^{LW}). The polar component was redefined by them as including all Lewis acid-base interactions (electron pair sharing interaction) in which a electron acceptor (acid) can accommodate an additional pair of electrons while a electron donor (base) can provide an unshared pair of electrons. They called this component the acid-base component, γ^{AB}. The total surface free energy is, therefore, given by: $\gamma^{\text{Total}} = \gamma^{LW} + \gamma^{AB}$.

They also defined two new components, $\gamma^{\oplus}$ and $\gamma^{\ominus}$, which are called the acid and base components of surface free energy, respectively. These components are related to the acid-base component of the surface free energy by:

$$\gamma^{AB} = 2\sqrt{\gamma^{\oplus}\gamma^{\ominus}}$$

The Lewis acidity (electron accepting capacity) or Lewis basicity (electron donating capacity) of a substance cannot by itself contribute to even the cohesion of the substance because of the absence of an electron donor or acceptor. But when a two-phase system exists, such as a fibre/marix interface, the acidity of one phase and the basicity of the other are complementary for each other and results in strong acid-base interactions (such a hydrogen bonding) across the interface, which can become a major contribution to the free energy of adhesion [2]. Hydrogen bonding is a typical example of Lewis acid-base interactions and accounts for most interactions between the functional groups of organic compounds or polymer phases.

Based on definitions, Good *et al.* [6,2] developed an acid-base theory to determine from contact angles the acid component of surface free energy, $\gamma^{\oplus}$, the basic component of surface free energy, $\gamma^{\ominus}$ and the dispersion component of surface free energy, γ^{LW}, of a solid. A general equation which relates the contact angle, Θ, of liquid l on solid s with the dispersion, acid and base components of surface free energy of the solid and liquid was proposed as follows:

$$\Upsilon_l(1 + \cos\theta) = 2(\sqrt{\Upsilon_s^{Lw}\Upsilon_l^{LW}} + \sqrt{\Upsilon_s^{\oplus}\Upsilon_l^{\ominus}} + \sqrt{\Upsilon_s^{\ominus}\Upsilon_l^{\oplus}}$$

To determine the γ_s^{LW}, $\gamma_s^{\oplus}$ and $\gamma_s^{\ominus}$ values of a solid by the above equation, a set of values γ^{LW}, $\gamma^{\oplus}$ and $\gamma^{\ominus}$ of three reference liquids, in which two are polar (water is preferred as one of these) and one is non-polar, are needed in order to create simultaneous equations to calculated the results using a computerized method [6, 2].

EXPERIMENTAL WORK

1. Materials and Preparations

The PP fibre used in this investigation is a monofilament fibre with a smooth surface, produced by direct extrusion of high molecular weight isotactic polypropylene. These PP monofilaments have rectangular cross section which ranges from 0.5 × 1.0 to 0.65 × 1.40 mm. The specific gravity, tensile strengh and elongation at break of the fibre are 0.91, 120 MPa and 14%, respectively. The oxyfluorinated PP fibres were prepared by conducting oxyfluorination reactions in an aluminum reactor using F_2/O_2 gas mixture at room temperature. To protect proprietary information exact details cannot be given, but treatments were done to different levels which are reported relative to the minimum treatment level. For hydrolysis of oxyfluorinated PP fibres, the oxyfluorinated fibres were immersed in distilled water for 2 hrs and then dried in air for 24 hrs. The cementitious matrices were made from a 80% cement-20% fly ash (by weight) mixture, dried natural river sand and crushed stone with a maximum size of 6 mm, according to following mixing ratio: Cement : Fly ash : Water : Sand : Crushed stone = 0.8 : 0.2 : 0.42 : 1.5 : 1.5.

2. Infra-Red Spectroscopy

The FTIR spectra were recorded on a infrared spectrometer fitted with a MTEC 200 photoacoustic accessory. During data collection, dry helium gas was used to purge the photoacoustic detector and dry nitrogen was used for the sample compartment and optics. The spectra obtained are the result of using a Happ-Genzel apodization function in the Fourier transformation of 128 sample scans with a wavenumber resolution of 8 cm^{-1}. The mirror velocity of the interferometer was set at 0.3165 $cm.s^{-1}$.

3. DCA Analysis and Calculation of Surface Free Energies

To obtain the surface free energies of ordinary and oxyfluorinated PP fibres, the contact angles of three reference liquids on the PP fibres must first be measured and then the simultaneous equations of acid-base contact angle theory are used to conduct the calculation. The contact angles, Θ, on the PP fibres were measured on a Cahn DCA-322 dynamic contact angle analyzer using the dynamic method, *i.e.* testing advancing and receding angles by the micro-Wilhelmy technique. A monofilament suspended from a microbalance is immersed into and then emersed from a liquid. According to the Wilhelmy relationship, the total force exerted on the fibre is the sum of wetting, gravitational and buoyancy forces [28], see Equation (1) below (here γ_1, C, d_1, y and A_f are surface free energy of the liquid, perimeter of the cross section of the fibre, density of the liquid, immersion depth and fibre cross-sectional area, respectively). The weight of fibre (mg) is tared out in the testing procedure and the buoyancy force is accounted for by extrapolating to zero immersion (such as in this investigation). Thus Equation (1) is simplified to Equation (2).

$$F = \gamma_1 C \cos \Theta + m_f g - d_1 g y A_f \tag{1}$$

$$F = \gamma_1 C \cos \Theta \tag{2}$$

As F γ_1 and C are either known or measurable, the cosΘ can be calculated. In this investigation, methylene iodide, water and ethylene glycol were used as testing liquids with the values of surface free energy components shown in Table I. The fibre perimeter was measured by a vernier caliper. Through one immersion and emersion cycle, the advancing and receding dynamic contact angles of the liquid on a PP fibre (Θ_a and Θ_r) were calculated. The average deviations for the advancing angles with 0.95 confidence are $\pm(0.5° - 1.4°)$, while for the receding angles are $\pm(0.3° - 1.2°)$. The testing laboratory was air conditioned with a temperature of approximately 25°C. The experiments were conducted on three specimens with one cycle each in three testing liquids for a specific type of fibre. The obtained Θ_a of three reference liquids on one type of fibre were applied to calculate surface free energy components by a programmed method.

TABLE I Surface free energy components (mJ/m^2) of the test liquids

Liquid	γ^{Total}	γ^{LW}	γ^{AB}	$\gamma^{\oplus}$	$\gamma^{\ominus}$
Water	72.8	21.8	51	25.5	25.5
Ethylene glycol	48.2	29	19	1.92	47
Methylene iodide	49.5	49.5	0	0	0

4. Fibre Pull-Out Test

Fibre pull-out tests were conducted using a dumbell-shaped specimen prepared by casting concrete into a custom-made mould with a PP fibre embedded in the middle [5], see Figure 1. The embedment length was 20 mm each in two sides and double plastic sheets with a hole in the middle were used to prevent the bonding between the two parts. Twenty four hours after casting, the specimens were released from the mould and then water cured for 28 days at 23 ± 2°C before testing. The pull-out tests were performed on a motor driven Monsanto tensometer at an extraction rate of 10 mm/min. The shear bond strength was calculated using the following equation: $\tau_{\text{bond}} = P/(CL)$. Here P, C

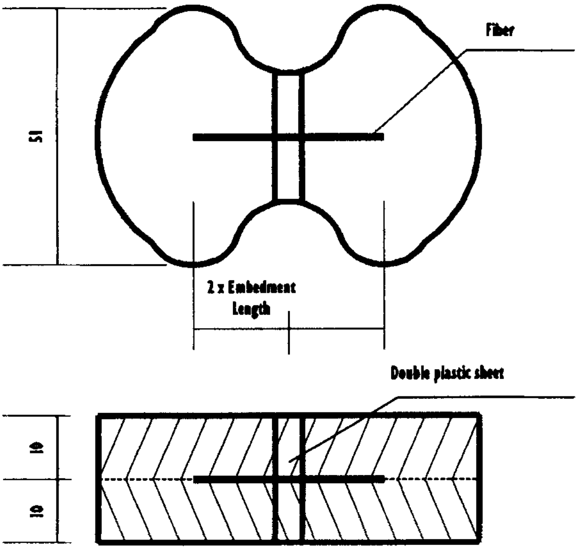


FIGURE 1 Sketch of pull-out test specimen.

and L are the maximum pull-out force, perimeter of cross-section of the fibre and bonding length, respectively.

RESULTS AND DISCUSSION

The advancing and receding contact angles of nonpolar methylene iodide ($\gamma^{AB} = 0$), strong polar (hydrogen bonding) water ($\gamma^{AB} = 51.0$ mJ/m^2) and medium polar ethylene glycol on the oxyfluorinated and hydrolyzed oxyfluorinated PP fibres surface compared with those on unmodified PP fibre are presented in Tables II and III. The standard deviations calculated are also reported in the Tables (values in brackets). The advancing contact angles were used to calculate the surface free energy components, according to the equations proposed by Good *et al.* [6]. The surface free energy components of the oxyfluorinated PP fibres with different oxyfluorination treatment levels compared with those of unmodified PP fibre (treatment level = 0) are shown in Table IV.

It can be seen from Tables II and III that the wettability of the PP fibre surface by water and ethylene glycol is largely increased (indicated by a large reduction in advancing and receding contact angle)

TABLE II Advancing contact angles, Θ_a, of water, methylene iodide and ethylene glycol on various PP fibre surfaces with different oxyfluorination treatment levels (value in brackets refers to standard deviation)

Treatment level	*1*	*2*	*8*	*20*	*30*	*60*
			Water			
Unmodified			105°(0.33)			
Oxyfluorinated	75°(1.8)	72°(0.22)	62°(0.25)	61°(3.1)	57°(0.3)	60°(0.05)
Oxyfluo-hydrolyzed	70°(0.62)	75°(0.75)	73°(4.3)	70°(1.2)	71°(1.6)	72°(0.94)
			Methylene iodide			
Unmodified			67°(0.47)			
Oxyfluorinated	62°(0.44)	63°(1.4)	64°(0.19)	63°(0.4)	67°(1.9)	69°(0.28)
Oxyfluo-hydrolyzed	65°(0.45)	64°(2.1)	62°(1.3)	63°(1.4)	64°(1.0)	64°(0.28)
			Ethylene glycol			
Unmodified			77°(0.87)			
Oxyfluorinated	43°(1.9)	44°(0.35)	46°(2.2)	43°(2.2)	41°(1.9)	47°(1.4)
Oxyfluo-hydrolyzed	52°(2.1)	55°(1.2)	47°(3.0)	47°(2.2)	45°(0.8)	49°(0.41)

TABLE III Receding contact angles, Θ_r, of water, methylene iodide and ethylene glycol on various PP fibre surfaces with different oxyfluorination treatment levels (value in brackets refers to standard deviation)

Treatment level	*1*	*2*	*8*	*20*	*30*	*60*
Water						
Unmodified			84°(1.2)			
Oxyflourinated	33°(0.68)	35°(2.5)	31°(2.0)	34°(2.3)	29°(1.4)	33°(1.0)
Oxyfluo-hydrolyzed	35°(1.0)	38°(0.77)	34°(1.6)	32°(1.9)	34°(1.9)	35°(0.87)
Methylene iodide						
Unmodified			51°(0.62)			
Oxyfluorinated	41°(1.2)	43°(0.25)	44°(2.6)	46°(1.5)	46°(0.18)	48°(2.0)
Oxyfluo-hydrolyzed	47°(1.1)	44°(0.32)	46°(0.2)	39°(0.4)	44°(0.01)	39°(0.42)
Ethylene glycol						
Unmodified			59°(4.4)			
Oxyfluorinated	23°(2.6)	24°(9.6)	30°(9.5)	30°(0.8)	27°(1.4)	32°(8.4)
oxyfluo-hydrolyzed	27°(0.98)	29°(3.0)	27°(3.3)	28°(1.0)	29°(0.39)	27°(0.54)

TABLE IV Surface free energy components (in mJ/m^2) of oxyfluorinated and hydrolyzed oxyfluorinated (*) PP fibres with different oxyfluorination treatment levels compared with that of unmodified PP fibre (treatment level = 0)

Level	γ^{LW}		γ^{AB}		$\gamma^{\oplus}$		$\gamma^{\ominus}$		γ^{totoal}	
		*		*		*		*		*
0	24		0.35		0.16		0.19		24	
1	27	25	8.3	7.9	2.1	0.90	8.3	17	35	33
2	26	26	9.3	6.1	1.9	0.74	12	13	35	32
8	26	27	10	6.7	1.1	0.88	24	13	35	34
20	26	26	11	8.7	1.2	1.3	25	15	37	35
30	24	26	13	9.2	1.4	1.7	29	13	37	35
60	23	26	11	7.9	1.1	1.2	28	14	34	34

through oxyfluorination while the wettability by a non-polar liquid such as methylene iodide is, in general, slightly increased after oxyfluorination. The increase in wettability arises from the large increase in the surface free energy components γ^{AB}, $\gamma^{\oplus}$ and $\gamma^{\ominus}$ by oxyfluorination of PP fibres, see data in Table IV. This contributes most to the increase in wettability of PP fibres by polar liquids due to the possible stong acid-base interactions between the PP fibre surface and polar liquids. Hydrolysis of oxyfluorinated PP fibres reduces the wettability by polar liquids compared with oxyfluorinated PP fibres because in general the γ^{AB}, $\gamma^{\oplus}$ and $\gamma^{\ominus}$ values have been reduced by hydrolysis. The wettability of oxyfluorinated PP fibres in non-polar liquids is not obviously influenced by hydrolysis. The reason is that although hydrolysis of oxyfluorinated PP fibres changes the C=O groups into —COOH groups, which reduces the polarizability of C=O double bond and, thus, the dispersion component γ^{LW} due to the conjugation effect discussed above, the number of F atoms PP molecular chains are also reduced by hydrolysis because of the change from acid fluoride groups to carboxyl groups, which increases the dipersion component, γ^{LW}, of PP fibres [29].

The results in Table IV show that the $\gamma^{\oplus}$, $\gamma^{\ominus}$, γ^{AB}, γ^{LW}, and, thus, the γ^{total} values of PP fibre, are largely increased by oxyfluorination treatments. The reason for this has been discussed in the above introduction section. The $\gamma^{\ominus}$ and, thus, the γ^{AB} values, gradually increase as the treatment level increases. This is due to the increase of C=O groups as the treatment level becomes higher. Photoacoustic spectra indicate that, at higher treatment level, C=O exhibits higher intensity, see Figure 2. After hydrolysis of oxyfluorinated PP fibres, the $\gamma^{\ominus}$ is largely

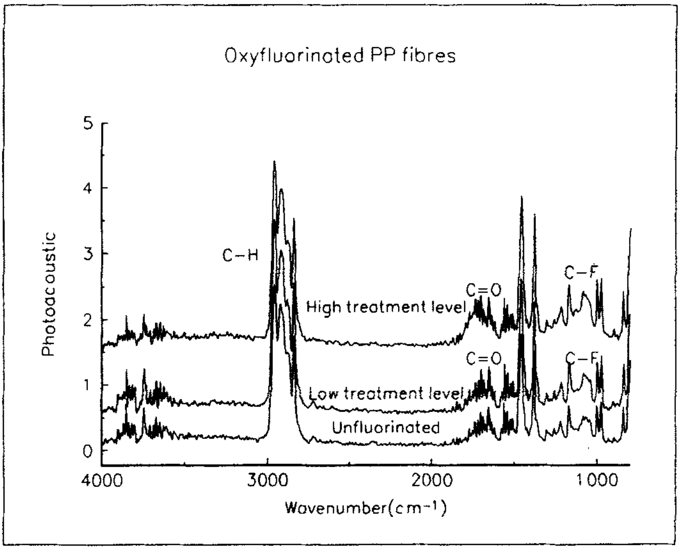
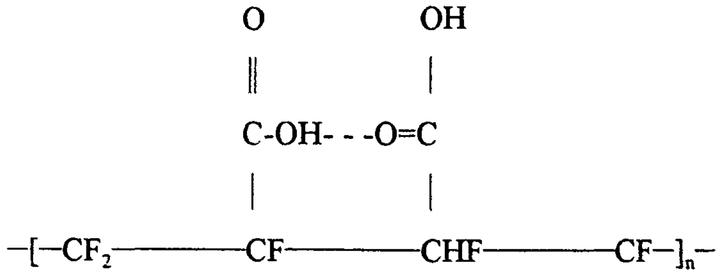


FIGURE 2 Photoacoustic infrared spectrum of oxyfluorinated PP fibres compared with unfluorinated PP fibre.

decreased because of the change from high Lewis basic C=O groups to strong Lewis acidic —COOH groups, which is also a main reason for the decrease of γ^{AB} after hydrolysis. Hydrolysis does not obviously change the γ^{LW} due to the opposite effects of reduced polarizability of C=O double bonds in —COOH groups, which reduces the γ^{LW}, and reduced F atom content in PP molecular chains, which increases the γ^{LW}. Although hydrolysis results in strong acidic —COOH groups which is supposed to increase the $\gamma^{\oplus}$ values, the results in Table IV indicate that the $\gamma^{\oplus}$ of oxyfluorinated PP fibres do not show an increase, and at some levels even decreases, after hydrolysis. This is because for oxyfluorinated polypropylene of this particular structure, after hydrolysis, the authors think that maybe the following structure exists:



$$\begin{array}{ccccc} & \text{O} & & \text{OH} & \\ & \| & & | & \\ & \text{C} & \text{-OH- - -O=} & \text{C} & \\ & | & & | & \\ -[-\text{CF}_2 & \text{—CF} & \text{—} & \text{CHF} & \text{—CF}-]_n- \end{array}$$

STRUCTURE 2

This kind of inter hydrogen bonding between two neighbouring —COOH groups may largely reduce the Lewis acidity of the hydrolyzed oxyfluorinated PP fibres.

The data in Tables II, III and IV do not seem to indicate a regular relationship between the treatment level and Θ or γ. This is mainly due to the fact that direct oxyfluorination of PP fibres results in a rough surface with strong microscopic heterogeneity, which can benefit the interfacial bonding by enhancing mechanical interlocks, see Figures 3 and 4. It can be seen that after oxyfluorination patches or bands with high roughness and irregularity are created at the fibre surface which, according to Good [6], leads to different (low or high) energy component spots on the PP surfaces. This kind of roughness or irregular energy patches can also affect the hysteresis of contact angles and thus the Θ_a and Θ_r measurement according to the Wentzel equation [30].

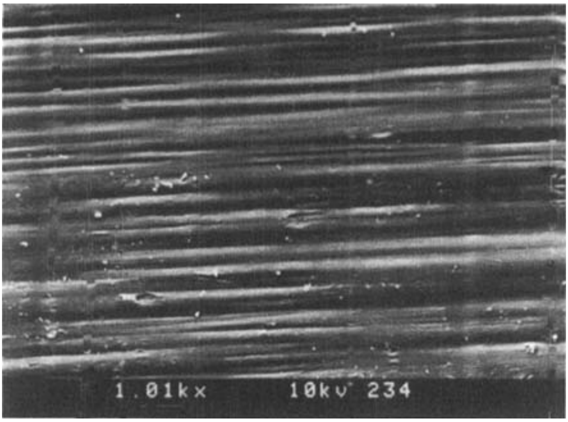


FIGURE 3 Microscopic picture of unmodified PP fibre surface (× 1000).

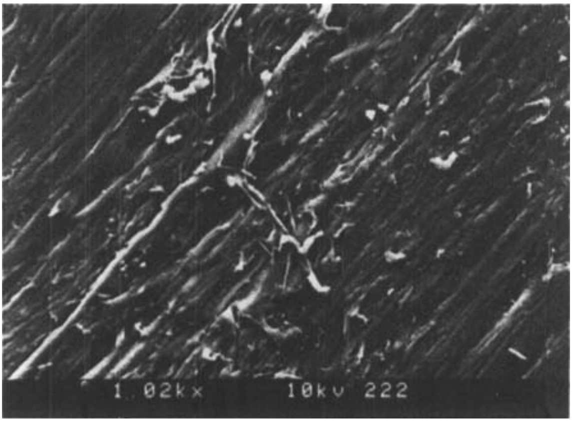


FIGURE 4 Microscopic picture of oxyfluorinated (treatment level 1) PP fibre surface (× 1000).

Interfacial shear bond strengths (average of three test results) of oxyfluorinated and hydrolyzed oxyfluorinated PP fibres with concrete matrix obtained by pull-out tests are shown in Table V. Results in Table V indicate that the interfacial bond strengths of oxyfluorinated PP fibres are obviously higher than that of unmodifed PP fibre. Maximum shear bond strength exists for certain conditions, for example, treatment level 1 produces the highest bond strength among all

TABLE V Shear bond strengths between concrete matrix and oxyfluorinated and hydrolyzed oxyfluorinated PP fibres with different oxyfluorination treatment levels

Treatment level	*Bond strength (oxyfluorinated)*	*Bond strength (hydrolyzed)*
0	0.19 MPa	0.19 MPa
1	0.45 MPa	0.23 MPa
2	0.41 MPa	0.21 MPa
8	0.30 MPa	0.16 MPa
20	0.32 MPa	0.22 MPa
30	0.36 MPa	0.35 MPa
60	0.36 MPa	0.29 MPa

oxyfluorination treatment levels. Hydrolysis of oxyfluorinated PP fibres reduces the interfacial bond strengths between the PP fibres and concrete matrix. Combining the results in Tables II, III and IV with Table V, it can be seen that the increase in bond strengths arises from a large increase of γ^{AB}, $\gamma^{\oplus}$ and $\gamma^{\ominus}$ after oxyfluorination. Increased wettability of PP fibres by polar liquids such as water also benefits the interfacial bonding. Although the shear bond strength data also exhibit an irregular relationship with treatment level, generally higher $\gamma^{\oplus}$ values lead to higher interfacial bond strengths. Hydrolysis of oxyfluorinated PP fibres reduces the bond strengths because hydrolysis reduces the $\gamma^{\ominus}$ and, thus, the γ^{AB} values, as well as the wettability by water, of the oxyfluorinated PP fibres. SEM observations of PP fibre/concrete interfaces show that oxyfluorinated PP fibres possess more intimate bonding with the concrete matrix, which arises from chemical bonding and good wetting, see Figure 5. The bondings between the unmodified PP fibres and concrete matrix is loose without intimate contact due to the poor wetting of the PP fibre surface and lacking in chemical bonding, see Figure 6. The microscopic observations of oxyfluorinated and unmodified PP fibres obtained from pull-out tests are presented in Figures 7 and 8, respectively. It can be clearly seen that unmodified PP fibre pulled out from concrete matrix has a smooth surface, while oxyfluorinated PP fibre pulled out from concrete possesses a rough surface with cementitious materials or cement hydration products attached to it, indicating a strong fibre/concrete interfacial bonding.

In order to understand the nature of intermolecular interactions between the oxyfluorinated PP fibres and cementitious matrix, inter-

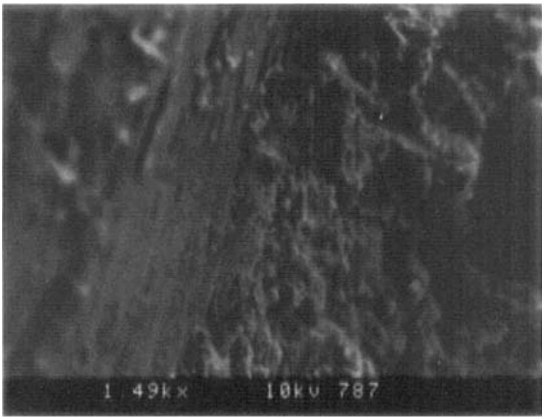


FIGURE 5 Microscopic picture of the interface between the oxyfluorinated PP fibre and concrete matrix (× 1500).

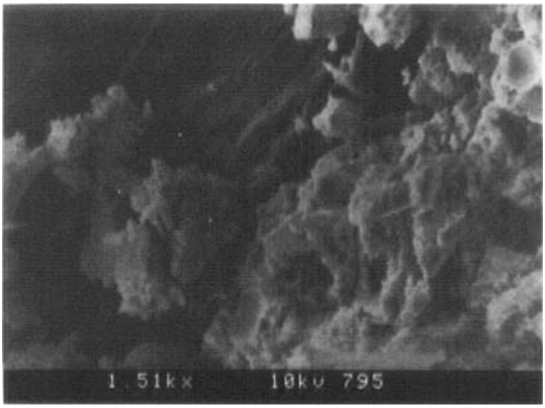


FIGURE 6 Microscopic picture of the interface between the unmodified PP fibre and concrete matrix (× 1500).

facial bond strengths of oxyflorinated and hydrolyzed oxyfluorinated PP fibres are correlated with surface free energy components. The shear bond strengths are plotted *versus* the $\gamma^{\oplus}$, $\gamma^{\ominus}$, γ^{AB}, γ^{LW} and γ^{total} of oxyfluorinated PP fibres and the correlation factors of straight line fits are 0.96, 0.042, 0.39, 0.29 and 0.54 respectively, see Figures 9, 10, 11, 12 and 13. Therefore, it is obvious that the molecular interactions

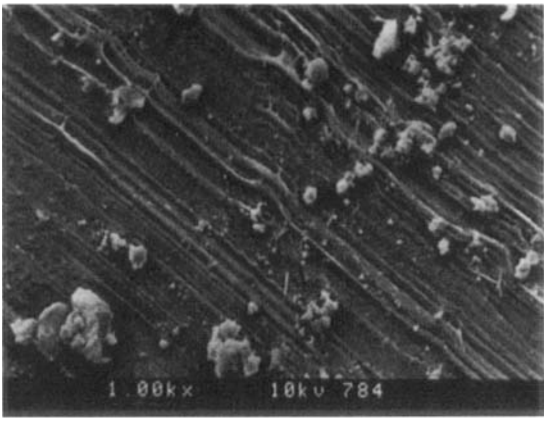


FIGURE 7 Microscopic picture of the fibre surface of oxyfluorinated PP fibre obtained from pull-out test (× 1000).

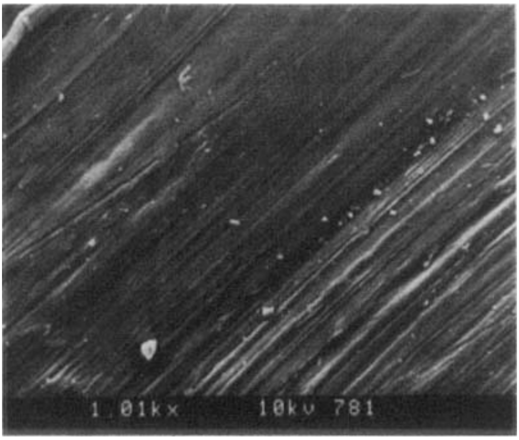


FIGURE 8 Microscopic picture of the fibre surface of unmodified PP fibre obtained from pull-our test (× 1000).

between oxyfluorinated PP fibres and cementitious matrices are best correlated with $\gamma^{\oplus}$ of the PP fibre surfaces with a correlation factor of straight line fit of 0.96, while the correlations between the bond strengths and γ^{AB}, $\gamma^{\ominus}$, γ^{LW} and γ^{total} can not correctly describe the molecular interactions in the PP fibre/concrete interfaces investigated in this project. This is due to the fact that the concrete matrix

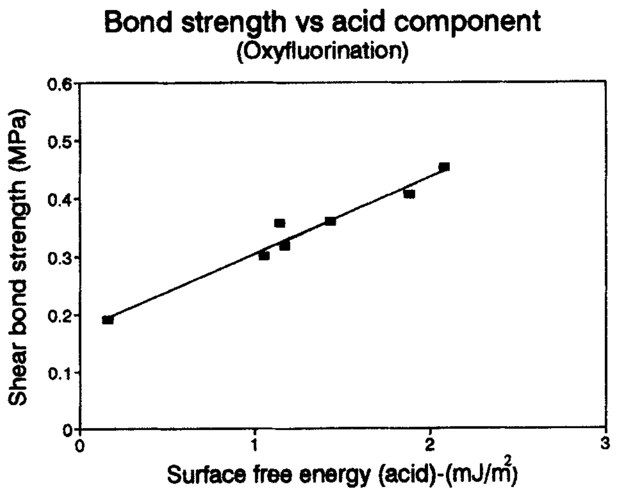


FIGURE 9 Correlation between the interfacial bond strength and the acid component of surface free energy of the oxyfluorinated PP fibres.

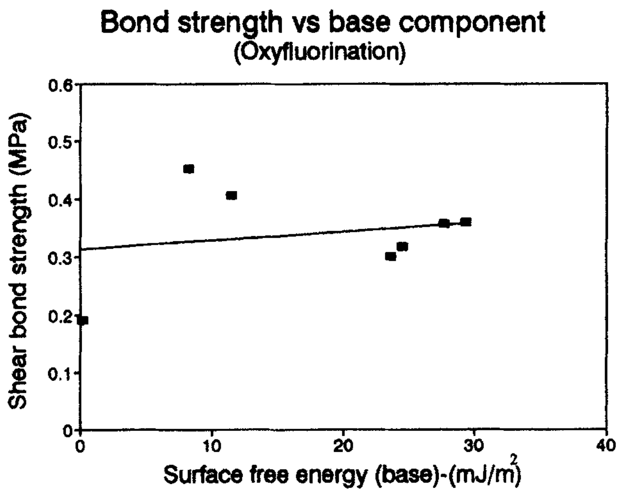


FIGURE 10 Correlation between the interfacial bond strength and the base component of surface free energy of the oxyfluorinated PP fibres.

possesses strong Lewis basicity arising from the groups such as OH$^-$ and SiO$_4^{4-}$, etc., existing in the cement hydration products, which can interact with increased acidity of oxyfluorinated PP fibres, resulting in

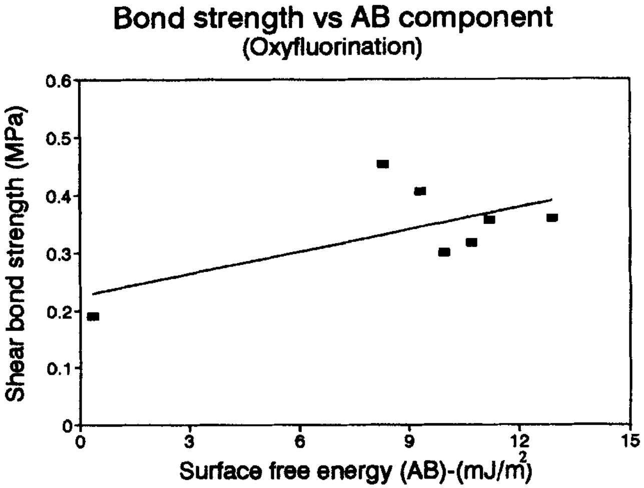


FIGURE 11 Correlation between the interfacial bond strength and the acid-base component of surface free energy of the oxyfluorinated PP fibres.

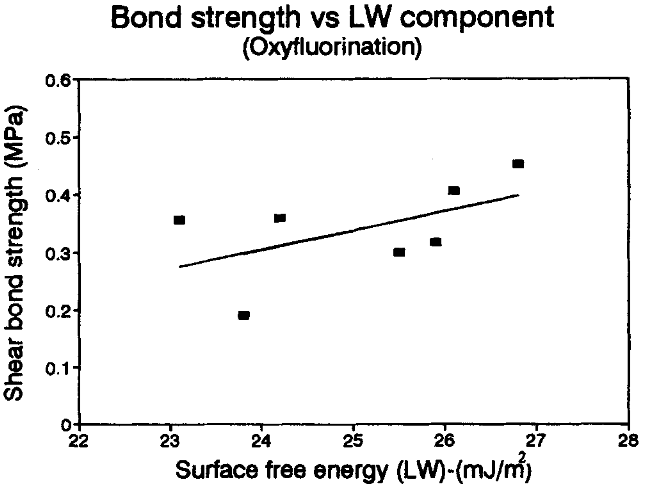


FIGURE 12 Correlation between the interfacial bond strength and the Lifshitz-van der Waals component of surface free energy of the oxyfluorinated PP fibres.

strong acid-base interactions. The very poor correlation between the bond strength and $\gamma^{\ominus}$ probably indicates that there is no adequate acidity existing in cementitious matrix to result in an acid-base

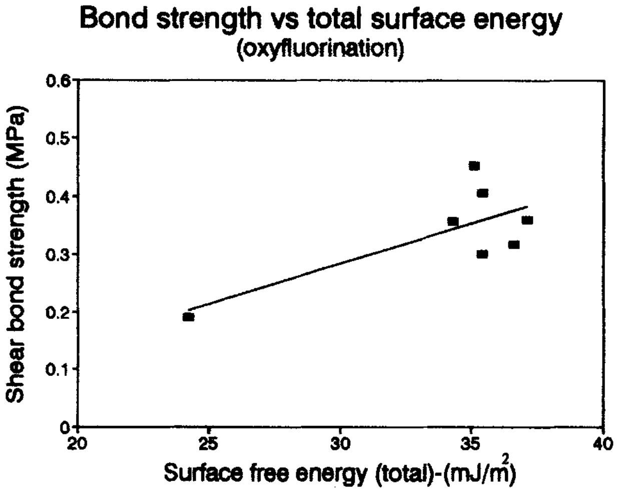


FIGURE 13 Correlation between the interfacial bond strength and the total surface free energy of the oxyfluorinated PP fibres.

interaction. After oxyfluorinated PP fibres are hydrolyzed, the correlations with all the surface free energy components become poorer, with correlation factors of 0.55, 0.068, 0.29, 0.001 and 0.18 respectively, see Figures 14, 15, 16, 17 and 18. This is because hydrolysis treatment leads to decrease in $\gamma^{\oplus}$, $\gamma^{\ominus}$ and γ^{AB} and, thus, the acid-base interactions between the PP fibre and concrete matrix are weakened. However, after hydrolysis, the interfacial shear bond strengths are still best correlated with $\gamma^{\oplus}$ of the PP fibres, with the best correlation factor of 0.55 among all.

CONCLUSIONS

1. Surface oxyfluorination increases the wettability of PP (polypropylene) fibres by polar liquids such as water, while the wettability of PP fibres by non-polar liquids is not obviously changed by the oxyfluorination treatment. Hydrolysis post-treatment reduces the wettability of oxyfluorinated PP fibres by polar liquids. Wettability is not necessarily increased as oxyfluorination treatment level is increased.

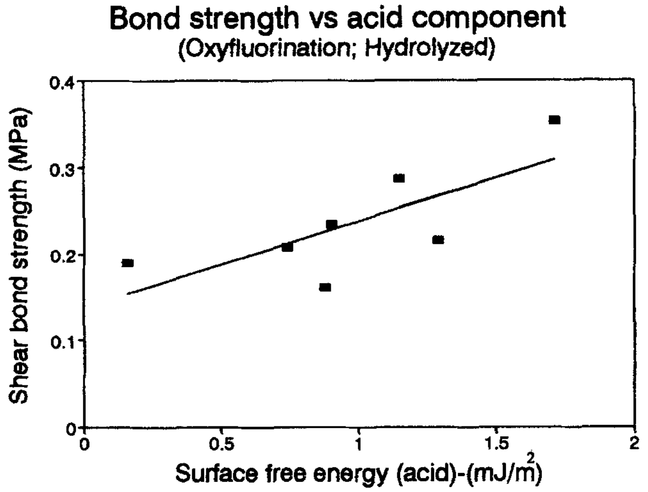


FIGURE 14 Correlation between the interfacial bond strength and the acid component of surface free energy of the hydrolyzed oxyfluorinated PP fibres.

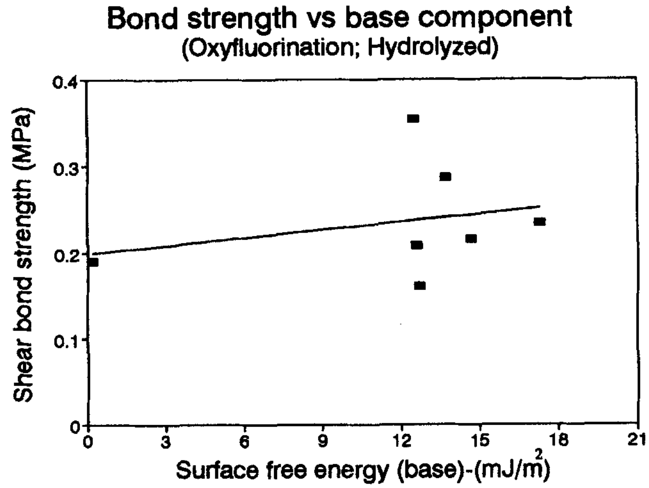


FIGURE 15 Correlation between the interfacial bond strength and the base component of surface free energy of the hydrolyzed oxyfluorinated PP fibres.

2. γ^{LW}, γ^{AB}, $\gamma^{\oplus}$, $\gamma^{\ominus}$ and γ^{total} of PP fibres are largely increased by oxyfluorination for either low or higher treatment levels compared with unmodified PP fibres. Hydrolysis post treatment generally

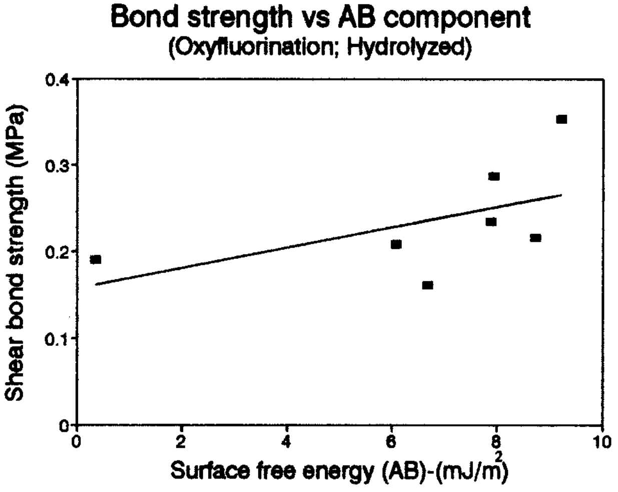


FIGURE 16 Correlation between the interfacial bond strength and the acid-base component of surface free energy of the hydrolyzed oxyfluorinated PP fibres.

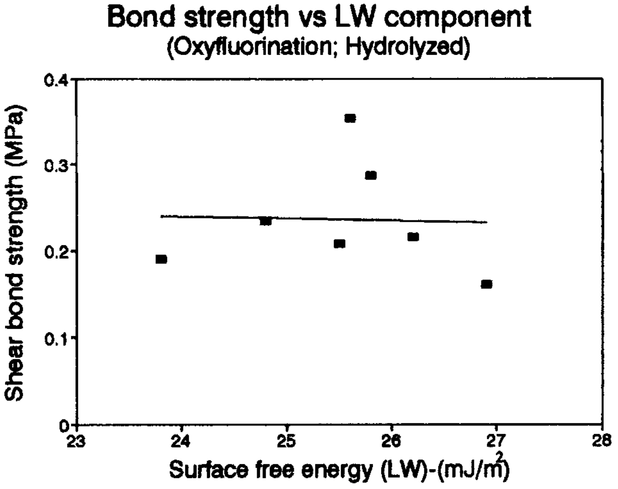


FIGURE 17 Correlation between the interfacial bond strength and the Lifshitz-van der Waals component of surface free energy of the hydrolyzed oxyfluorinated PP fibres.

decreases the values of all the surface free energy components due to the reduction of C=O group content and the restriction of polarizability of C=O double bond in —COOH groups after

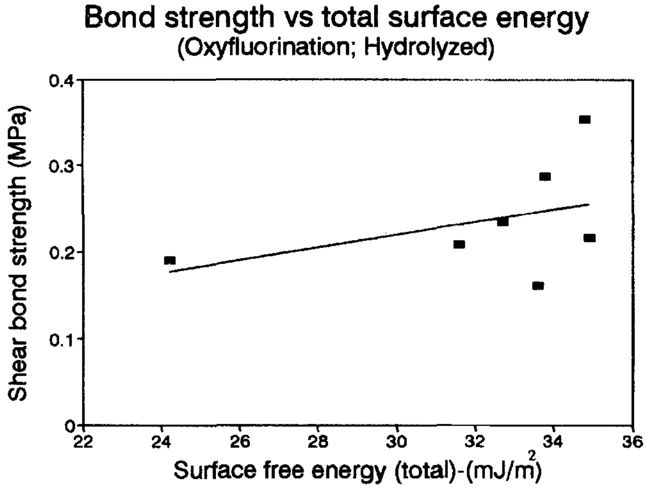


FIGURE 18 Correlation between the interfacial bond strength and the total surface free energy of the hydrolyzed oxyfluorinated PP fibres.

hydrolysis. The interfacial shear bond strengths between various oxyfluorinated PP fibres with different oxyfluorination treatment levels and cementitious matrix are enhanced compared with unmodified PP fibres. Hydrolysis of oxyfluorinated PP fibres will reduce such interfacial bonding improvement.

3. Interfacial bond strengths are better correlated with $\gamma^{\oplus}$ values of PP fibres while the correlations with γ^{LW}, $\gamma^{\ominus}$ and γ^{total} are poorer. This indicates that the intermolecular interactions between the PP fibres and cementitious matrices mainly arise from the acid-base interactions between the increased Lewis acidity of oxyfluorinated PP fibres and the high Lewis basicity of cement hydration products.
4. Oxyfluorination also increases the micro-roughness of PP fibre surfaces which benefits the fibre/concrete mechanical interlocking but may affect contact angle measurement and contributes to the irregular relationship between the data of fibre surface free energy components and the surface treatment level.

Acknowledgment

The authors gratefully acknowledge the support and help of Mr. C. J. J. Wilke and Mr. J. P. Le Roux from the Atomic Energy Corporation of South Africa Limited. The support from South African Fibrecrete (Pty.) Ltd., as well as from its Managing Director Mr. A. W. Louw, is also very much appreciated.

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