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Air-plasma treated polyethylene fibres: effect of time and temperature ageing on fibre surface properties and on fibre–matrix adhesion

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The effect of a low energy air-plasma treatment of extended chain polyethylene (ECPE) fibres (Spectra®900) on the adhesion with a matrix of epoxy resin has been studied. Surface energies of fibre and matrix were calculated by contact angles, measured with a Wilhelmy microbalance in different liquids, and the adhesion between fibres and the matrix was evaluated through a pull-out test. The results showed an increase in fibre–matrix adhesion by a factor of ca. 1.5 calculated by surface energy measurements, and by a factor of ca. 4 measured by the pull-out tests. Time (up to six months) and temperature (in the range 20–120 °C for 2 h) ageing caused some decrease in adhesion with respect to the values evaluated just after the fibre plasma treatment. The plasma treatment did not affect the fibre's mechanical properties.

1. Introduction

Mechanical performance of a composite material depends strongly on fibre–matrix adhesion at the interface. In spite of their good mechanical properties, some fibres possess quite inert surfaces limiting the effectiveness of the stress transfer between the matrix and fibre due to a weak interface.

This is the case for ECPE fibres produced by melt or gel-spinning, which reach a tensile modulus between 70 and 100 GPa and a tensile strength of 2.5 GPa, and are inert in many chemically hostile environments and do not release toxic monomers or oligomers. Despite these impressive properties and, therefore, their high potential interest as reinforcing fibres for the fabrication of high performance polymeric matrix composites, ECPE fibres have an inert, non-polar surface from which poor adhesion to most resins results. For this reason many attempts have been made to modify the ECPE surface by chemicals [1], grafting [2], glow discharge [3], corona discharge [4] or cold plasma [5–22]. In Table I some of the methods and results of research groups using the cold plasma method are reported.

In many cases, however, treatments with high plasma power and with gases which are very aggressive with respect to the fibre surface, such as ammonia or pure oxygen, have been used, producing the desired increase in adhesion properties, but at the expense of fibre mechanical integrity.

In the literature, only a few papers report the use of air as the plasma gas in the treatment of ECPE, in spite of the fact that air is safe to stock and easy to handle in industrial applications. Moreover, adhesion of modified ECPE fibres have mainly been analysed by pull-out tests, lacking extended contact angle data and surface tension calculations.

Another point requiring further clarification is the effect of the ageing on plasma modification. Morra *et al.* [23] showed that, on plasma treated polypropylene, the initial strong reduction in contact angle was temporary and that the surface free energy of the material returned to lower values after a few days (i.e. the contact angle increased).

In this paper the result of a low power air-plasma treatment on surface modification of ECPE fibres, determined by dynamic contact angle measurements and surface energy calculations is reported. Moreover, the effect of modification on the adhesion of fibres to an epoxy resin matrix, evaluated by theoretical adhesion work determination and experimental fibre pull-out tests in single fibre microcomposites is discussed. The effect of time and/or temperature ageing on the fibre surface properties are also reported. A morphological scanning electron microscopy (SEM) analysis of the fibre surface after treatment is presented, with the origin and evaluation of micropits appearing on the fibre surface commented upon.

2. Experimental procedure

2.1. Materials

ECPE or UHMWPE (ultra high molecular weight polyethylene) fibres (Spectra® A900) gel-spun were obtained from Allied Signal Inc., having a nominal

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TABLE I Summary of plasma treatments on ECPE fibres reported in the literature

Ref.	Fibre	Matrix	Plasma gas	Plasma data	Tests	Notes
5	Drawn from Unifoss 2912 at different λ	Ciba-Geigy XD927	O_2	10 J s^{-1}, 10 min, 10 ml min^{-1}	PO, TS, SEM	
6	Drawn from Unifoss 2912 at different λ Celanese yarn	Ciba Geigy XD927, Code 91	O_2	40 J s^{-1}, 10 min, 66.7 Pa, 17 ml min^{-1}, 60 J s^{-1}, 10 min, 80 Pa, 20 ml min^{-1}	ILSS, UFS, FM, TM, TS, CS, CIT, SEM, Env	
7	Drawn from Unifoss 2912 at different λ	Ciba Geigy XD927	O_2	50 J s^{-1}, 10 min, 50 Pa, 17 ml min^{-1},	SEM, PO, CALD, TS	CALD: resin and glycerol
			$O_2 + H_2O$	50 J s^{-1}, 5 + 5 min, 50 Pa, 17 ml min^{-1}		
8	Drawn from Unifoss 2912 at λ = 30 Drawn from Alathon 7030 at λ = 30	Ciba Geigy XD927	O_2,	30–60 J s^{-1}, 0.5, 10 min, 10, 60 ml min^{-1}	PO, SEM	
			He	20, 200 J s^{-1}, 0.5, 10 min, 20, 60 ml min^{-1}		
			Ar	20, 200 J s^{-1}, 0.5, 10 min, 10, 40 ml min^{-1}		
			CF_4	20–100 J s^{-1}, 0.5, 10 min, 10, 50 ml min^{-1}		
9	Fabric made by Spectra® 900 (Allied-Signal)	DER331-DEH26	NH_3	50–150 J s^{-1}, 1–10 min	PT, SEM, CALD, TS	CALD: water
10	Celanese Snia Tekmilon Spectra 1000 Drawn from Unifoss 2912 at λ = 30	Ciba-Geigy Araldite LY1927 (XD927)	O_2	120 J s^{-1}, 2 min, 53.3 Pa, 17 ml min^{-1}	ILSS, FS, UFS, TS, TM, CS, SEM, FD, GC, CALD	CALD: resin
11, 12	Spectra® 900	DER331-DEH26	CH_2CHCH-NH_2	45, 70 J s^{-1}, 20, 40 min, variable flux, 66.7 Pa	TS, CA?, PO, SEM, VFD	Polymer forming treatment
13	Drawn from Alathon 7030 at λ = 30	Ciba-Geigy Araldite LY 1927 (XD927)	O_2	50, 120 J s^{-1}, 2–5 min, 53.3 Pa, 17 ml min^{-1}	TS, TM, UFS, PO, CA, LD, GC, SEM	CALD: resin, water
14	Spectra® 1000	Epon828-DDM	NH_3	100 J s^{-1}, ? min, 33.3 Pa, 20 ml min^{-1}	ILSS, ILFE, FM, FS, TBIP, SEM	
15, 16	Spectra® 900, Spectra® 1000	PMMA	Ar, N_2, CO_2	30 J s^{-1}, 1–10 min, 33.3–40 Pa	CAWM, DSC, XPS, SEM, VFD, PO, TS	CAWM: ethylene glycol
17	Spectra® 1000	DER331-DEH26	O_2	60 J s^{-1}, 5 min, 66.7 Pa, 10 ml min^{-1}	XPS, SEM, CALD, ATR-IR, TS, PO	CALD: epoxy resin, glycerol
18	Spectra® 1000	LLDPE	O_2	60 J s^{-1}, 5 min, 66.7 Pa, 10 ml min^{-1}	XPS, SEM, CALD, ATR-IR, TS, PO	CALD: epoxy resin, glycerol *Trans*-crystallinity
19	?	?	Air, O_2	350 J s^{-1}, 66.7 Pa,	ILSS	
20	?	?	Various	50 J s^{-1}, 10 min, 66.7 Pa		
21	?	?	?	?	TS, ILSS, PO,FS, FM, CA?	
22	?	?	Not reported	< 350 J s^{-1}, 33.3–113.3 Pa, 254 ml min^{-1}	TS, TM, ILSS, FS, FM, CA?	
This work	Spectra® 900	CHEM-RES-E95-PGF24	Air	20 J s^{-1}, 30 min, 40–53.3 Pa, 10 ml min^{-1}	SEM, PO, DSC, DMTA, CAWM, OFD, WMFD, XPS	CAWM: water, methylene iodide Time–temperature ageing

PO = pull-out; TS = tensile strength; SEM = scanning electron microscopy; ILSS = interlaminar shear strength; UFS = ultimate fracture strength; FM = flexural modulus; TS = tensile strength; CS = compressive strength; CIT = Charpy impact tests; Env = environmental tests; CALD = contact angle by liquid drop; PT = peel test; GC = gel content; OFD = optical filament diameter; VFD = vibroscopic filament diameter; CAWM = contact angle by Wilhelmy microbalance; WMFD = Wilhelmy microbalance filament diameter; ILFE = interlaminar fracture energy; TBIP = transverse ballistic impact properties; DSC = differential scanning calorimetry; XPS = X-ray photoelectron spectroscopy; ATR-IR = attenuated total reflectance IR; ? = information not available; CA? = method not specified for the reported contact angle.

diameter of 38 μm. The diameter value was revised using two techniques, namely, optical microscopy (on five different samples scanned along their length 90 times each in order to provide a significant statistic distribution of the fibre diameter) and contact angle analysis. In the latter case, ten different fibre samples were immersed in *n*-heptane (assumed to have contact angle equal to 0°, with the fibre) and the fibre wet perimeter, p, calculated by the equation:

$$F = p\gamma\cos\theta = p\gamma$$

where F is the force measured on the balance and γ is the known n-heptane surface tension. The results indicated fibre diameters of 43 ± 8 μm or of 43 ± 4 μm measured by optical microscopy and the Wilhelmy microbalance, respectively, in agreement with the data (42 ± 4 μm) calculated by the fibre cross-section measurements performed by other authors [15] using a vibroscopic technique [27]. It is worth noting that contact angle analysis gave more accurate values than microscopy [25]. A fibre diameter of 43 μm was assumed throughout the data analysis presented here.

Before use fibres were washed in a detergent solution, rinsed in distilled water and then run under vacuum to eliminate any possible contaminant.

The matrix was a bisphenol-A epoxy resin (CHEM RES E95 by Henkel), having a Brookfield viscosity of 400–650 mPa·s at 25 °C and an equivalent epoxy molecular weight of 180–195 g mol^{-1}.

PGF 24 curing agent (by Henkel) with a Brookfield viscosity of 200–500 mPa·s at 25 °C was used at a weight percentage ratio of 1:2. After 2 h at 90 °C the resin appeared fully reticulated, with a $T_g = 39.1$ °C, as shown by differential scanning calorimetry (DSC) analysis.

Contact angles were measured in HPLC grade water (Merck), methylene iodide, reagent grade (Merck-Schuchardt) and n-heptane, reagent grade (Carlo Erba).

2.2. Plasma apparatus

The plasma apparatus, assembled in this laboratory, consisted of a glass cylinder reactor (500 mm in length and 150 mm in diameter) equipped with semicylindrical copper electrodes. A radiofrequency generator RF5S (maximum power 500 J s^{-1} and frequency 13.56 MHz) matching network AM-5 and controller AMNPS-2A supplied by RF Plasma Products, (Marlton, NJ, USA) were used.

Vacuum, produced by a double stage rotative pump, was controlled and measured by Edwards devices; in particular, the manometer transducer was the Barocell 600. The working pressure was ca. 1 Pa.

The plasma operating power, 20 J s^{-1}, was chosen in accordance with Ref. [6]. At this power level preliminary tests (done in this laboratory on LDPE) suggest best results were obtained for a treatment time of 30 min, therefore this was used for the fibres; air flowed along the reactor axis at a flow rate of 10 ml min^{-1}.

After treatment fibres were stored in a desiccator at room temperature until use.

2.3. Contact angle measurements

Contact angles were measured using the Dynamical Wilhelmy Microbalance model 322 by Cahn; this microbalance, which is fully automated and computer controlled, has a precision of ± 1 μg and an immersion speed variable in the range 2–256 μm s^{-1}. Speeds of 2 μm s^{-1} and 20 μm s^{-1} were used for fibres and epoxy resin samples, respectively; in each case the immersion depth and the environment test chamber temperature were equal to 20 mm and 20 ± 2 °C, respectively.

Surface tensions of liquids were measured using a glass plate, whose surface was activated in air plasma at 100 J s^{-1} for a few minutes.

2.4. SEM and optical microscopy measurements

Morphology analysis was performed using a Cambridge Stereoscan 200 scanning electron microscope and an Ortholux II POL-BK (Leitz) optical microscope equipped with a PERTEL image analyser.

2.5. Mechanical measurements

2.5.1. *Fibre strength*

Tensile strength of a single fibre was measured by a Polymer Laboratories MINIMAT tensile testing machine with a 20 N load cell at an elongation rate of 60 mm min^{-1}, on fibres (gauge length = 25 mm) fixed at both ends around specially made conical tabs attached to the clamps (Fig. 1a). Each reported value is an average of ca. 30 measurements.

2.5.2. *Dynamic mechanical thermal analysis*

Tensile dynamic mechanical tests were performed in a DMTA MK II (Polymer Laboratories) dynamic mechanical thermal analyser, from − 100–150 °C at a frequency of 5 Hz and a heating rate of 2 °C min^{-1}.

2.5.3. *Interfacial shear strength*

The fibre–resin interfacial shear strength was determined by measuring the force (F_p) to completely displace a fibre from a small disc of cured matrix (Fig. 1b). Samples of treated fibres were prepared the same day as plasma treatment, by passing a single

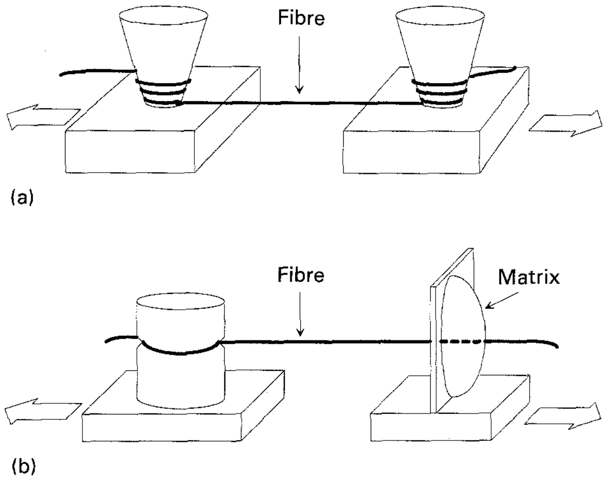

Figure 1 The conical tabs (specially made) used to clamp the fibres for tensile tests (a) and details of microcomposites clamping system (b).

ECPE fibre through a cardboard tab and putting a small drop of the liquid resin on it around the fibre. The embedded fibre length (L) ranged from 0.7 to 1.2 mm. The resin curing was done at a temperature of 90 °C for 2 h.

The interfacial shear strength (τ_i) was evaluated according to:

$$\tau_i = \frac{F_p}{\pi d L}$$

where d is the fibre diameter.

Tests were carried out using the Polymer Laboratories MINIMAT tensile testing machine at room temperature (20 ± 2 °C) and at the elongation rate of $10\,\text{mm}\,\text{min}^{-1}$. For each experimental situation at least 25 samples were tested.

In order to measure how the ageing time affected the interfacial shear strength, τ_i was evaluated at 5, 10, 15, 20 and 25 days after the fibre plasma treatment and the preparation of microcomposites. In this case at least 15 samples were tested for each experimental point.

3. Results

SEM micrographs of ECPE fibres, prior to and after, air-plasma treatment are shown in Fig. 2. As reported [8, 10, 13], the plasma caused the formation of "micropits", visible on the surface of the treated fibre, exhibiting different sizes and shapes, dependent on plasma operating parameters. These micropits, whose direction is generally perpendicular to fibre axis, were never observed on untreated fibres, indicating that they resulted from the plasma treatment and not from the SEM electron beam energy, as has been suggested [15]. It is worth noting that after one week the size of micropits had reduced significantly and after six months they had disappeared: consistent with this, Nardin and Ward [7] observed that the micropits which had larger sizes in plasma treated ECPE fibres with higher draw ratios did not form if fibres were annealed before plasma treatment. The formation of micropits is therefore assumed to be due to the presence of internal stresses in the fibre surface. Due to micropit formation, a decrease in mechanical properties, as well as an increase in fibre–matrix adhesion (due to higher mechanical interlocking) could be expected.

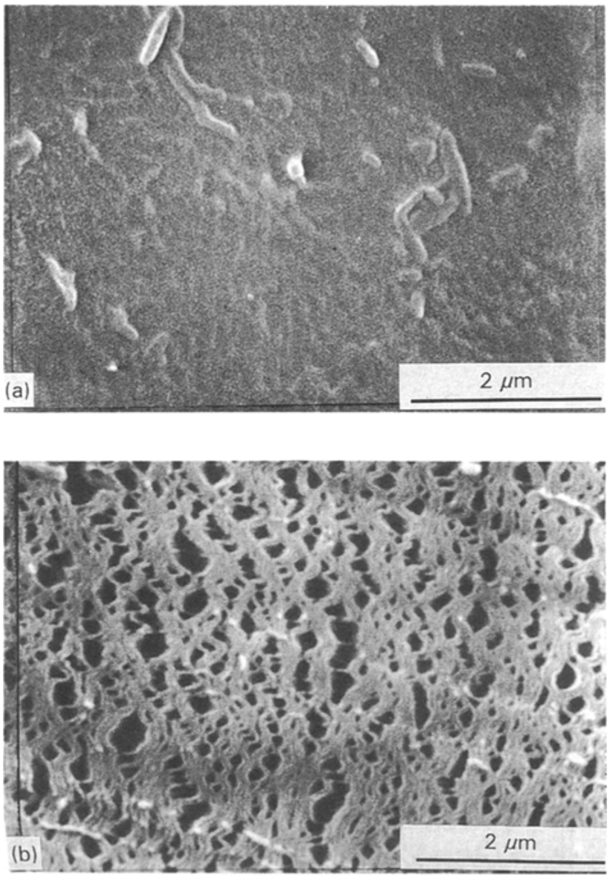

Figure 2 SEM images of a Spectra® 900 fibre surface as received (a), and air-plasma treated ($20\,\text{J}\,\text{s}^{-1}$, 30 min, $10\,\text{ml}\,\text{min}^{-1}$) one day after treatment (b).

Mechanical characterization of fibres, however, did not show any difference between treated and untreated fibre tensile strength (2.55 GPa), indicating that the size of micropits is small compared to the fibre intrinsic defects. Moreover, dynamic mechanical thermal analysis did not show any difference between the two kinds of fibres; in fact, the DMTA curves are quite good, overlapping in all ranges of test temperature. However, as is widely reported in the literature (see for example Ref. [28]) loss modulus, E'', or tan δ peak, appears at 70 °C. This peak is due to an α transition, connected to chain-fold rearrangement [28–30], which may affect the thermal stability of the plasma treated ECPE fibres surface.

Advancing and receding contact angles, measured in water, of fibres before and after plasma treatment are given in Table II. Data for the epoxy matrix and for fibres aged for different times at different temperatures are also reported in Table II. The advancing contact angles are plotted in Figs. 3 and 4 as function of ageing time and temperature, respectively. The effect of plasma treatment on fibres wettability is very marked, showing a large increase in both advancing and receding contact angles. After a few days the contact angles increased slightly, but thereafter the values were much smaller than the initial ones, even after six months. The treatment of fibres for 2 h at 60 °C had only a slight effect; the effect, however, was much larger if the temperature was raised to 90 °C (i.e. to a temperature higher than α, the observed polyethylene transition), triggered by the increase of the polymer molecular mobility, due to some extent to the observed α transition. The α transition effect cannot be distinguished from the data in Fig. 4, and requires confirmation by further investigation and measurements on fibres aged at temperatures lower, around and higher than that of the observed transition.

Contact angles measurements were also run in methylene iodide, in order to calculate the fibre and epoxy resin surface energies by using the harmonic [26] and the geometric [26] mean equations. Values of calculated energies and adhesion work are collected in Table III.

Both harmonic and geometric equations result in a clear increase of the total fibre surface energy after

TABLE II Advancing and receding contact angles of the epoxy matrix and of Spectra® 900 fibres before and after air-plasma treatment (30 min at 20 J s^{-1}; air flux = 10 ml min^{-1})

Material	Conditions	Liquid	θ_{adv}	θ_{rec}
Epoxy matrix		Water	63 ± 3	13 ± 3
Epoxy matrix		Methylene iodide	48 ± 3	0 ± 3
Untreated ECPE		Water	90 ± 3	76 ± 3
Untreated ECPE		Methylene iodide	57 ± 7	54 ± 8
Plasma treated ECPE	Mean value after 1 day	Water	42 ± 4	10 ± 5
Plasma treated ECPE	Mean value after 1 day	Methylene iodide	32 ± 6	17 ± 6
Plasma treated ECPE	Mean value after 14 days	Water	49 ± 4	19 ± 8
Plasma treated ECPE	Mean value after 180 days	Water	60 ± 4	30 ± 5
Plasma treated ECPE	Kept at 60 °C for 2 h	Water	47 ± 4	–
Plasma treated ECPE	Kept at 90 °C for 2 h	Water	56 ± 4	–
Plasma treated ECPE	Kept at 120 °C for 2 h	Water	75 ± 3	40 ± 3

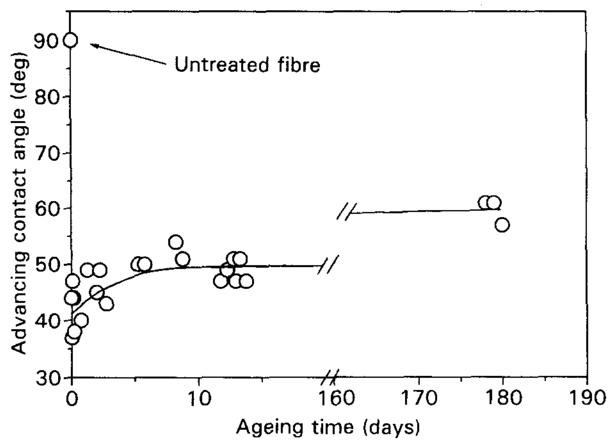

Figure 3 Advancing contact angles (°) of plasma treated Spectra® 900 fibres versus ageing time after treatment (in days). The value for the untreated fibre is also reported.

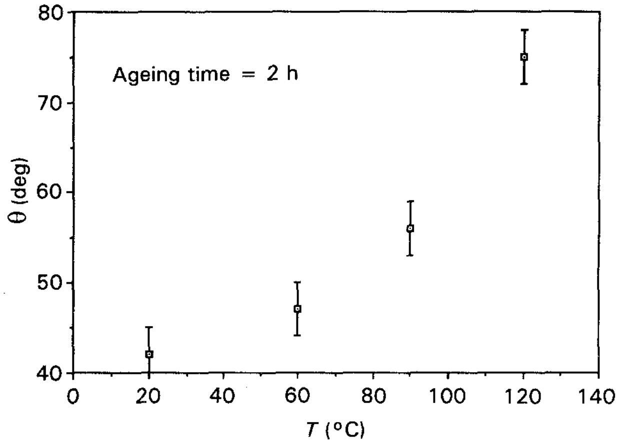

Figure 4 Advancing contact angles (°) of plasma treated Spectra® 900 fibres versus temperature (°C) of a 2 h ageing treatment.

TABLE IIIa Surface energies of matrix and fibres calculated from experimental contact angles by geometric and harmonic mean methods. γ, γ^d, γ^p, are the total surface energy, the dispersive component and polar component, respectively; while x^p represents the polarity, i.e. the ratio between the polar component and the total surface energy

	Surface energies (mJ m^{-2}) Harmonic mean method				Surface energies (mJ m^{-2}) Geometric mean method			
	γ	γ^d	γ^p	x^p	γ	γ^d	γ^p	x^p
Epoxy resin	46	25	21	0.46	45	29	16	0.35
Untreated spectra	32	25	7	0.22	31	28	3	0.10
Treated spectra	60	30	30	0.50	60	34	26	0.43

TABLE IIIb Total adhesion work, W_{tot}, and its polar and dispersive components, W_p and W_d, respectively, between resin and fibre before and after the plasma treatment

	Adhesion work (mJ m^{-2}) Harmonic mean method			Adhesion work (mJ m^{-2}) Geometric mean method		
	W_{tot}	W_d	W_p	W_{tot}	W_d	W_p
Before plasma treatment	72	51	21	70	57	13
After plasma treatment	104	55	49	103	63	40

plasma treatment, with differences for the polar and dispersive energy components being very small, as calculated by the two methods. The effect of the plasma treatment on the polar component of the surface energy appears to be much larger with respect to the effect on the dispersive component.

The increase in the calculated dispersion component of surface energy (ca. 20%) could not be correct, being indebted to the formation of micropits and so instead indicating an increase of the fibre real surface area (by a corresponding 20%); in fact, the contact angle hysteresis (i.e. the difference between the advancing and receding contact angles) after the treatment increased, thus attesting [31] an increment of the fibre surface roughness, as also shown by the high magnification SEM observation (see Fig. 2).

The very high increase of the surface energy polar components (also, in this case, these energies have been calculated with respect to the nominal initial fibre surface area and, hence, following our previous assumption, are overestimated by 20% for the treated fibres) attest the polar nature of the atoms or groups that have been exposed to the fibre surface, as confirmed by the detection of oxygen and nitrogen on the surface of air plasma treated polyethylene sheets [16] or fibres [32] by XPS.

The previous comments apply similarly to the reported components of the adhesion work (see Table IIIb); the total increase of ca. 50% is mainly due to the polar component and the results obtained by the harmonic or geometric mean methods are very similar.

Interfacial shear strength data, obtained by pull-out tests, are shown in Fig. 5 as a function of ageing time for plasma treated ECPE fibres. The reference measured τ_i value for untreated fibres was 2.44 ± 0.15 MPa. After a little, but measurable decrease (only 3%) in the first five days, τ_i remained substantially constant.

Comparison of Figs 3 and 5, show that τ_i and γ behave similarly, both being due to the rearrangement of polymer molecules on the fibre surface. However, in microcomposites preparation (i.e. samples used for the interfacial shear strength measurements) fibres underwent 2 h treatment at 90 °C, which should correspond to a significant decrease in the fibres wettability (i.e. increase of contact angle from 42 to 56°), as reported in Fig. 4. A reasonable hypothesis is that the polar resin, to some extent, inhibits the molecular rearrangement in the fibre surface, both during microcomposite curing and its storage.

4. Conclusions

The described air-plasma treatment increases the surface energy of ECPE fibres and the adhesion work between the ECPE fibres and the epoxy matrix. No modification of mechanical properties of fibres was detected, notwithstanding the presence of micropits on the modified fibre surface.

It is interesting to note that the micropits, which are visible at a magnification of ca. 17 000 ×, were visible only on treated fibres, so clearly resulted from the treatment and not the SEM electron beam, as reported elsewhere [15].

The surface energy of epoxy resin is higher than the surface energy of untreated Spectra 900® fibre, corresponding to an high contact angle and to poor adhesion; after treatment the situation changed markedly and the fibre surface energy became higher than the epoxy one; this last situation should correspond to a complete wetting of the fibre from the matrix and, hence, to good adhesion. The reported variations of surface energies agree well with the marked improvement of the interfacial shear strength, measured between untreated and plasma treated fibres, and by the 50% adhesion work increase.

The surface of treated fibres, especially if stored in air, is not thermodynamically stable; the outer layer fibre molecular conformation rearranges, kinetically dependent on the storage temperature. Interfacial shear strength analysis confirm that in a polar medium (the epoxy matrix) the situation is possibly different; in fact, the reduction of shear strength is lower.

From the results presented the following conclusions can be drawn:

1. Low power plasma treatment in air is able to increase the adhesion work of ECPE fibres to epoxy matrices to a level obtained by other gases, e.g. oxygen [5–7], without inducing variations of mechanical properties of fibres;
2. The treatment induces modifications sufficiently stable with time; however, some ageing exists and, therefore, it is better to reduce the time interval between the plasma treatment and the production of the composite; storage of fibres at low temperatures is advisable.

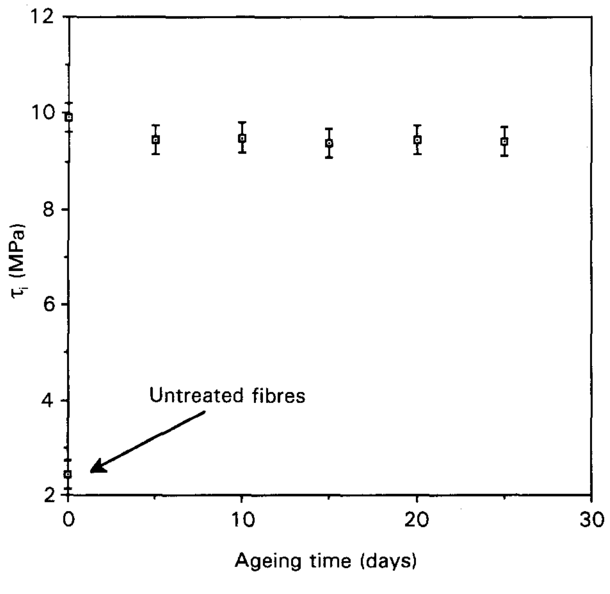

Figure 5 Values of interfacial shear strength (MPa) versus time after treatment (days) in composite of Spectra® fibres air-plasma treated and epoxy matrix.

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