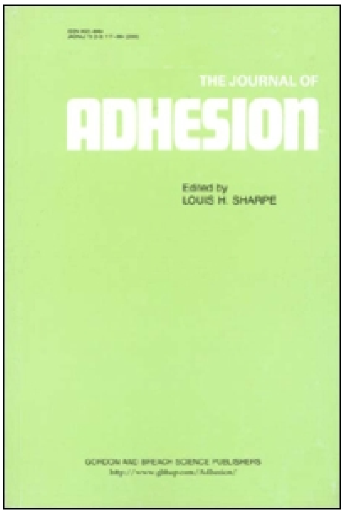

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STUDY OF BONDED PLASMA-TREATED POLYETHERIMIDE COMPONENTS FOR POWER INTEGRATION: DURABILITY IN A HOT/WET ENVIRONMENT

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STUDY OF BONDED PLASMA-TREATED POLYETHERIMIDE COMPONENTS FOR POWER INTEGRATION: DURABILITY IN A HOT/WET ENVIRONMENT

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This work deals with the study of the durability, in a hot/wet environment, of structural adhesively bonded polyetherimide (PEI) assemblies used in power electronics packaging technology. An overall approach is proposed, for which the epoxy joint-PEI substrates assembly on the one hand, and the adhesive system components (substrate surface and bulk adhesive) on the other hand, are studied separately with different analytical techniques. The first part of this work was devoted to the substrate surface state and to its modification using a cold plasma treatment of the PEI surface. Then for chosen parameters (power, duration) contact angle

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measurements indicated an increased surface tension resulting from surface decontamination (removal of release agent and carbon contaminants) and from the creation of polar species, such as esters or carboxylic acid groups, on the PEI surface (XPS analyses). The second part of this study concerned the bulk adhesive ageing in an ethylene glycol-water solution at 70°C. Mass uptake measurements versus time showed the liquid diffusion in the bulk adhesive associated with a microscopic damage of the epoxy system. An overall plasticizing of the adhesive with a considerable decay of the α-transition temperature of one of the two adhesive epoxy-amine networks (TGDDM-BAPP) was also highlighted using rheometry. However, in these ageing conditions, the adhesive glassy modulus decreases slighty because of the thermomechanical stability of the other epoxy network. In the third part, the asymmetric wedge test showed the beneficial effect of the cold plasma treatment on the epoxy/PEI interface durability in the aggressive medium.

Keywords: Polyetherimide; Cold plasma treatment; Epoxy adhesive; Rheometry; Humid ageing; Asymmetric wedge test

INTRODUCTION

Power integration (or hybrid technology) can be simply summarized by “more power in less space.” In power converters used on the railway traction drives this results in compact modules, inside which all the elements required for energy transformation are gathered close to the power chips. The increase in density of electronic components that results from this integration leads to the use of innovative materials and the definition of new assembly processes, in addition to cooling problems (Figure 1). Combining high heat resistance with high strength and broad chemical resistance, polyetherimide is an engineering thermoplastic of great interest for the power electronics packaging technology, especially as a water collector used in cooled converters.

Reliability of adhesive joints in a hot/wet environment (such as antifreeze fluid at 70°C) is an important concern, and attention must be paid to joint ageing. As a prerequisite for yielding high adhesive bond strength and durability in hot/wet environments, an effective surface pretreatment, an adhesive with chemical resistance against aggressive media, and a tool for evaluating interface degradation (presumed locus of failure) are usually needed. On the basis of this report, an overall approach [1] has been proposed to optimize and study the durability of the PEI/adhesive interface by separately considering the components of the adhesive system (substrate surface, bulk adhesive, joint). Specifically, we did the following:

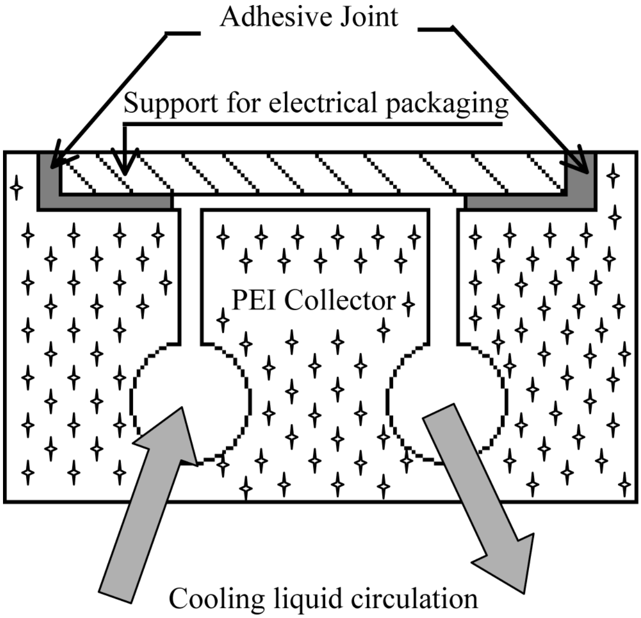


FIGURE 1 Diagram of the cross section of the power converter cooling device.

1. ***Increase the adhesion properties of polyetherimide by cold plasma and characterize the influence of the treatment on the surface state of substrates and on the mechanical resistance of joints.*** Cold plasma treatment is a known and efficient tool to improve the adhesion properties of thermoplastics. The properties of cold plasma are the result of the ionization of a neutral gas by electronic collisions. Highly reactive species such as free radicals, excited ions, or metastable molecules are produced, and which favour chemical reactions at the polymer surface [2]. The large amount of vacuum ultraviolet light also causes photochemical effects that could break many chemical bonds. The four major effects [3] resulting from the plasma–polymer surface interaction are *surface cleaning* by removal of organic contamination, *etching* by ablation of weak boundary layers, *crosslinking or branching* of the extreme surface by the creation of covalent bonds between polymer chains, and *surface chemical modifications* of the first layers (grafting reactions of specific functions leading to increase or decrease, according to the nature of the gas, of surface polarity and hydrophilicit). The affected thicknesses, which depend on the operating conditions (nature of gas, time, pressure, power, etc.) and on

the nature of substrates can vary from the first molecular layers (a few tens of Å) to some micrometers.

2. ***Evaluate the loss of physical properties of the bulk adhesive and the weakening of the polyetherimide/epoxy adhesive interface in the ageing medium (water/ethylene glycol mixture at 70°C).*** The cooling liquid diffusion within the adhesive joint is likely to weaken the joint resistance by reversible (plasticization, swelling, etc.) or irreversible (hydrolysis, cracking, etc.) degradation or by attack of the substrate/adhesive interface [4]. This bulk adhesive ageing is characterized by the determination of the sorption kinetics of the liquid and by rheometry for the variation of the adhesive's thermomechanical properties. However, the physical or chemical effects, due to water ingress within the adhesive, cannot explain fast failures due to joint delaminations. The adhesive/substrate interface is then suspected to be a special area where accelerating ageing factors concentrate [5]. This justifies the use of the asymmetric wedge test. This rupture test appears to be the most able to determine the combined effects of moisture, temperature, and applied stress, which are opposed to the durability of structural adhesive joints.

EXPERIMENTAL

Materials

Polyetherimide substrates reinforced with 30% short glass fibres (PEI; Ultem® 2300 GE Plastics, Evry, France) were supplied by GE Plastics. The chemical structure of polyetherimide is shown in Figure 2.

The adhesive used was EA 9392 from Loctite Aerospace (Bacf. Point, CA, USA). It contains two epoxy resin–amine hardener systems:

- TGDDM (Tetraglycidyl diamino diphenyl methane)–BAPP (Bis amino propyl piperazine)
- DGEBA (Diglycidyl ether of Bisphenol A)–EDA (Ethylene Diamine).

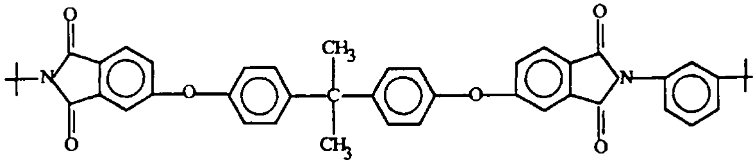


FIGURE 2 Polyetherimide chemical structure.

Inorganic fillers (silica and aluminium powders, 25% by weight), acrylonitrile butadiene styrene (ABS), and an elastomeric liquid phase (amine terminated butadiene nitrile; ATBN) are added to the resin. During the cure process the rubber phase separates, forming dispersed submicron-size particulates that enhance the adhesive toughness and its impact resistance. The adhesive was cured for 4 h at 80°C followed by a natural cooling of the oven to ambient temperature.

Surface Treatment

Before plasma treatment polyetherimide substrates were ultrasonically washed in 95% pure ethanol and rinsed in distilled water. This preparation was the reference surface state. Plasma treatment was carried out in a 60-l Glen Technologies (Fremont, CA, USA) reactor at frequency of 40 kHz with a maximum power of 1 kW. Samples were placed in the glow discharge. The plasma treatment consisted of two stages, a first discharge in argon and a second one in oxygen, both at a reduced pressure of about 20 Pa. The studied parameters were the power and the duration of both treatment cycles. In the following the nomenclature P (600 W, 150 s), for instance, will indicate a plasma treatment at a power of 600 W for 150 s.

The influence of plasma treatment on the superficial properties of substrates is, as a general rule, characterized under two major aspects: the description of the surface ablation and topographic modifications on the one hand, and the study of the superficial functionalization, generally analyzed by spectroscopic techniques and by wettability, on the other hand.

With our equipment and for limited power and duration, the plasma treatment did not induce topographic changes of PEI-roughened injection-moulded surfaces ($R_a \cong 1\,\mu m$, $R_t \cong 20\,\mu m$; roughness or scanning electron microscopy observations). The Scanning Electon Microscope used was the Jeol S35 from JEOL (EUROPE) S. A. (Croissy sur Seine, France). These changes exist, however, and they were observed by atomic force microscopy (VEECO Instruments Nanoscope III, VEECO Instruments, Dourden, France tapping mode in) on quarter micron-polished specimens. As for X-ray photoelectron spectroscopy (XPS) measurements, they were carried out with a Surface Science Instrument spectrometer (model 301; Kratos, Manchester, UK) using a focused monochromatised Al K_α radiation ($h\nu = 1486.6\,eV$). The residual pressure inside the analysis chamber was *ca.* 5×10^{-7}Pa. The peaks were recorded with a constant pass energy of 50 eV. The diameter of the irradiated area of the sample was 600 μm. Charging effects were minimised with a low energy (5 eV) electron flood gun in conjunction with a transmitting fine mesh proximity screen. The binding energy scale was calibrated from the C 1s peak at 285.0 eV, corresponding to carbon atoms of PEI bound only to carbon or hydrogen atoms. The XPS signals were analysed using a nonlinear background [6], and the fitting peaks of the experimental curves were calculated using a combination of Gaussian (80%) and Lorentzian (20%) distributions.

The surface free energy (dispersive and acid-base components) of PEI plasma-treated samples was determined by the sessile drop technique (Digidrop apparatus from GBX Instruments, Romans, France) using Fowkes calculation [7]. Four liquids were used, two polars (distilled water and ethylene glycol) and two dispersives (diiodomethane and α-bromonaphthalene).

Ageing of Bulk Adhesive

During service, the energy dissipated by the power chips heats the cooling liquid up to 70°C, a temperature that was used for all of our ageing experiments. This commercial cooling liquid was a monoethylene glycol (40% v/v)–distilled water mixture along with additives in low concentrations (corrosion inhibitors, colouring agent, antioxidant, etc.). The pH of this solution was 8.3.

The kinetics of sorption of the cooling liquid were determined on 6 parallelepiped samples ((10×10) mm^2, thickness of 2 mm). After several ageing times, samples were dried on paper and weighed using a Sartorius microbalance with a sensitivity of $\pm$ 10 µg. Three measurements were made for each sample. Thermogravimetric analyses were also carried out (TGA-50 apparatus, Shimadzu, Tokyo, Japan) under nitrogen (20 ml/min) and a temperature scan rate of 1°C/min. The influence of ageing on the thermomechanical properties of the bulk adhesive was evaluated using the ARES rheometer from Rheometric Scientific Marne, La Vallée, France. Thermomechanical studies of parallelepiped samples ($40 \times 10 \times 2$ mm^3) were performed with an imposed torsion strain at an angular frequency of 1 rad.s^{-1}, from 25°C to 250°C using a temperature scan rate of 2°C/min. The evolution of the dynamic viscoelastic parameters G' (*storage modulus* corresponding to the stored elastic energy), G'' (*loss modulus* equivalent to the energy dissipated within the material), after and the *damping* represented by the loss factor, tan delta ($= G''/G'$), were determined after the bulk adhesive ageing in the cooling liquid followed or not by desorption.

Interfacial Degradation of Joints

Two mechanical tests were used to characterize the degradation of joints in the cooling liquid: a shear test by compressive loading and an asymmetric wedge test.

Compression Single Lap Shear Test

The single lap shear test by compressive loading [8] was inspired by the ASTM D2293-69 test method.

In this test (Figure 3), a steel support fixed on the static test machine crosshead holds the bonded assembly vertically in a cavity with vertical sides. A squeezing screw fixes the lower adherend, and small wheels guide the upper adherend in the vertical direction to prevent rotation of the assembly due to the mechanical couple resulting from the eccentric loading applied by the movable test machine crosshead. The applied load is transmitted through a point contact by means of a steel hemisphere.

The single-lap assembly was composed of two PEI substrates whose dimensions were close to $(25 \times 25 \times 4)\ \text{mm}^3$ with a bonding area of $(13 \times 25)\ \text{mm}^2$. All shear tests were carried out using a test machine INSTRON (Instron, Canton, MA, USA) (loading speed of 2 mm/min for all the trials).

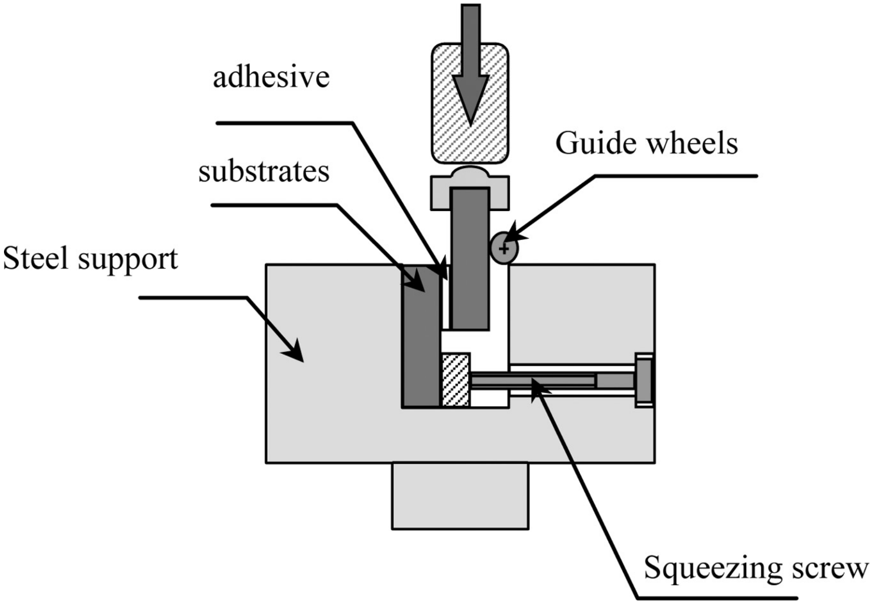


FIGURE 3 Diagram of the single-lap compression-shear test.

Asymmetric Wedge Test

The cleavage specimen was made of a polyetherimide substrate bonded, using EA 9392, to a 1.6 mm thick aluminium alloy (2024) blade (Figure 4). This blade was previously subjected to a phosphoric anodization in order to increase its adhesion properties and therefore to avoid aluminium/epoxy adhesive interface failures, a rupture locus without interest in our work. The dimension of the PEI substrates was about $(80 \times 15 \times 4)\ \mathrm{mm}^3$. An original device was then designed for the wedge insertion at the speed, generally employed for this test, of 10 mm/min. The wedge insertion caused the adhesive joint cracking with a crack deviation towards the studied interface to characterize its degradation during ageing. The specimen was then stored in a desiccator (20°C, 40% R.H.), for 24 h until the crack propagation stopped. Crack lengths on both sides of the cleaved specimens were then evaluated using a binocular on a table (x, y) displaced by micrometric screws. The immersion of the specimen in the ageing medium caused a new crack extension which was followed during the ageing time. Fracture energy was calculated using the relation in Equation (1), derived from the elastic foundation model [9, 10]:

$$G = \frac{3h^2E_1e_1^3E_2e_2^3}{8a^4}\left[\frac{E_1e_1^3C_2^2 + E_2e_2^3C_1^2}{\left[E_1e_1^3C_2^3 + E_2e_2^3C_1^3\right]^2}\right] \qquad (1)$$

$$C_i = 1 + 0,64e_i/a$$

where e_1, E_1, e_2 and E_2 represent the thicknesses and the Young's moduli of the aluminium blade and the PEI substrate, respectively; a represents the crack length; and h represents the wedge thickness.

RESULTS AND DISCUSSION

Surface Activation of Polyetherimide by Cold Plasma

For polymers, plasma/surface interaction results primarily from the action of UV radiation and from reactions induced by the chemistry

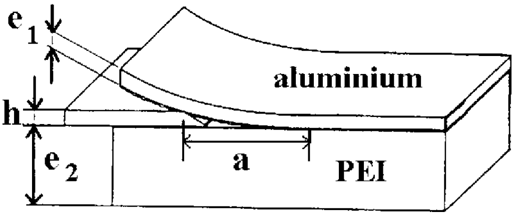


FIGURE 4 Schematic of the asymmetric wedge test.

of free radicals [3]. These macroradicals, once formed in ionized gas, break chemical bonds and produce recombination reactions or oxidations at the polymer surface. The improvement of adhesion properties of polymers, after plasma treatment, arises especially from the grafting of functional (polar) groups on the surface and increases superficial attractions between the polymer and the adhesive. Thus, the main goal of this first part of the study is to characterize treated PEI surfaces in terms of morphological modifications, polarity, and superficial oxidation and to correlate these surface-state evolutions with an increase in the adhesion properties of the substrates.

The atomic force microscopy (AFM) images in Figure 5 illustrate the evolutions of the PEI surface topography following plasma pretreatment. The surface state of polished polyetherimide, which constitutes our reference, shows underlying short glass fibres at the extreme surface (Figure 5a). Average roughness (R_a), limited to the swept zone (100 μm × 100 μm), is close to 20 nm with a maximum amplitude (R_t) of 190 nm. The surface morphology of the reinforced thermoplastic sample, treated by plasma (P (600 W, 150 s)), is somewhat different with the appearance of several peaks or asperities on the AFM image (Figure 5b) which leads to a new microroughness at the material surface. Average roughness, as a general guide, is about 45 nm with a maximum amplitude of 285 nm. Green [11] has previously reported the creation of similar asperities or nodules at the surface of a polypropylene irradiated by the ionization of a gas mixture plasma (nitrogen and oxygen).

The increase of the treatment time to 600 s (P (600 W, 600 s)) causes a thermostable matrix ablation leading to the air exposure of glass fibres. This selective ablation is so important that it is appropriate to visualize the profile on a 2 × scale in Z (Figure 5c). Blackmann *et al.* [12] highlighted an exposure of carbon fibres and an increase of roughness after an oxygen radio frequency plasma treatment of composites due to the ablation of polyetheretherketone (PEEK) and polyphenylene sulfide (PPS) thermoplastic matrices. This ablation or degradation is the consequence of chemical bond breaking and results, in general, in a weight loss of the sample and a release of molecular fragments in the gas phase.

On the other hand, for the same duration (150 s), the polymer ablation is more important at 800 W (Figure 5d) than at 600 W. Similarly, the surface ablation increases with the time of irradiation. This increase of ablation, according to the power, is due to the increase of both density and energy of the reactive species at the polymer surface. However, the ablation depth at 600 W for a long time (P (600 W, 600 s)) is nevertheless deeper than the one observed at 800 W (P (800 W, 150 s)).

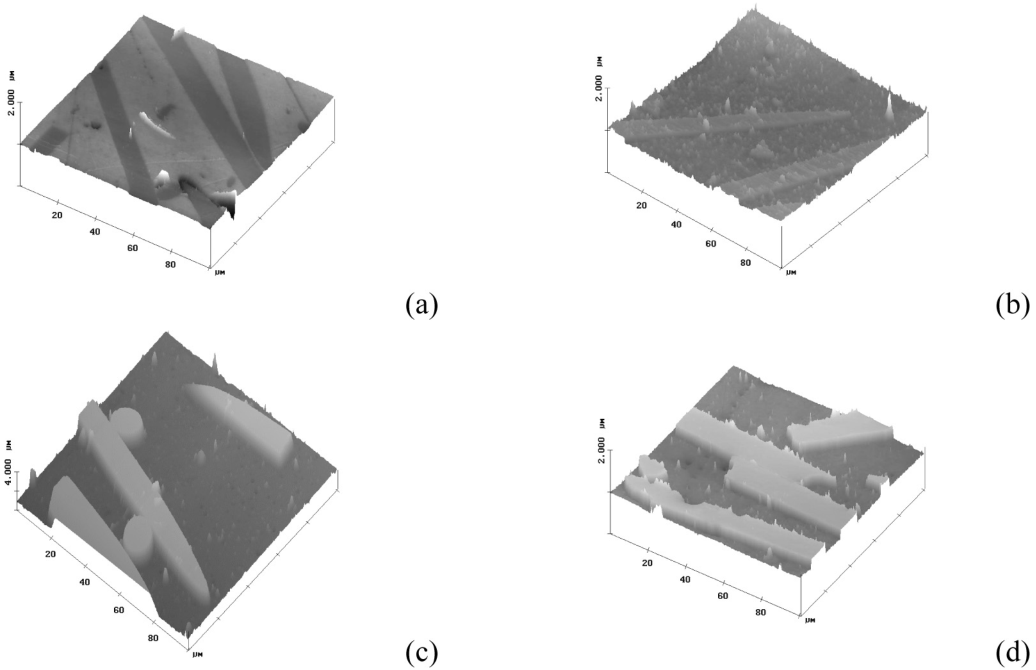


FIGURE 5 AFM 3-D surface (100 µm × 100 µm) images of PEI morphology: (a) degreased, (b) P (600 W, 150 s) (c) P (600 W, 600 s) (d) P (800 W, 150 s).

The major interest of the plasma, in our case, lies above all in the chemical functionalization of the PEI surface by grafting of polar species, in order to increase the adhesive/substrate adhesion. To confirm the oxidation and the increase of the PEI surface free energy, XPS and wettability analyses were carried out following plasma pretreatment according to the parameters time and power.

Table 1 presents the main XPS results (binding energy, full width at half maximum (FWHM), atomic % of various species) for degreased PEI and for plasma-treated surfaces according to the duration of the discharge. Similar results have been noticed according to the plasma power; consequently, only evolutions according to treatment time are discussed here.

XPS C 1s, O 1s and N 1s spectra of untreated PEI are in good agreement with the literature [13]. C 1s spectra obtained for degreased PEI and after 60, 150, and 600 s plasma treatment are shown in Figure 6.

As expected, the C 1s spectrum consists of three components (Figure 6a): a first one at 285.0 eV corresponds to C atoms bound only to C or H atoms, a second one at 286.3 eV corresponds to C atoms bound to one oxygen or one nitrogen, and a third one at 288.7 eV corresponds to C atoms bound to one oxygen and one nitrogen. The O 1s spectrum consists of two components: 532.1 eV corresponding to **O**=*C* oxygen atoms, and 533.7 eV correspond to *C*-**O**-*C* oxygen atoms. The N 1s spectrum consists of a unique component at 400.7 eV. The measured surface chemical composition C/O/N: 81/14/4.5 is very close to the expected one, 82/13/4.4, according to the molecular formula (Figure 2). The presence of a satellite peak (shake-up) at 291.6 eV in the C 1s spectrum can be attributed to multielectronic transitions involving $\pi-\pi^*$ transitions due to the aromatic rings [14].

Plasma treatment induces a change in chemical composition of the surface. The O/C ratio increases with sample exposure to the plasma reactor, from 17% for degreased PEI to 100% for the longest times (600 s). The N/C ratio is slightly decreasing and very weak. More precisely, the oxygen percentage increases whereas the carbon one decreases. This overall evolution of the chemical composition indicates that, after a long treatment time, the PEI surface is saturated by oxygen, and suggests that a competition between functionalization and degradation of the polymer takes place at the PEI surface.

When the treatment time increases, the component at 286–287 eV attributed to **C**-*O* and **C**-*N* carbon atoms increases. As the N/C ratio remains almost constant, this evolution can be attributed only to the formation of new C-O bonds. In the same way, the component observed at 288–289 eV increases, showing the formation of O=C-O bonds.

TABLE 1 XPS Analyses of PEI Surfaces According to Treatment Time of Plasma: Chemical Composition of the Surface and Binding Energy, FWHM and Relative Area of Components in C 1s and O 1s Spectra

		C 1s			O 1s		Composition		
		C-C **C**-H	**C**-O **C**-N	O-**C**=O N-**C**=O	**O**=C	C-**O**-C	%*C*	%*O*	%*N*
PEI degreased	Position (eV) *(FWHM)*	285.0 *(1.6)*	286.3 *(1.4)*	288.7 *(1.2)*	532.1 *(1.6)*	533.7 *(1.7)*	81	14	4.5
	Atom%	**76**	**17**	**7**	58	42			
PEI P (600 W, 60 s)	Position (eV) *(FWHM)*	285.0 *(1.4)*	286.5 *(1.5)*	288.8 *(1.5)*	532.1 *(1.8)*	533.2 *(1.8)*	74	23	2.7
	Atom%	**71**	**20**	**9**	63	37			
PEI P (600 W, 150 s)	Position (eV) *(FWHM)*	285.0 *(1.6)*	286.7 *(1.6)*	288.8 *(1.5)*	532.2 *(1.6)*	533.0 *(1.7)*	60	38	2.2
	Atom%	**71**	**19**	**10**	59	41			
PEI P (600 W, 600 s)	Position (eV) *(FWHM)*	285.0 *(1.6)*	286.5 *(1.7)*	288.5 *(1.7)*	531.8 *(2.3)*	533.4 *(1.9)*	49	49	1.7
	Atom%	54	35	11	80	20			

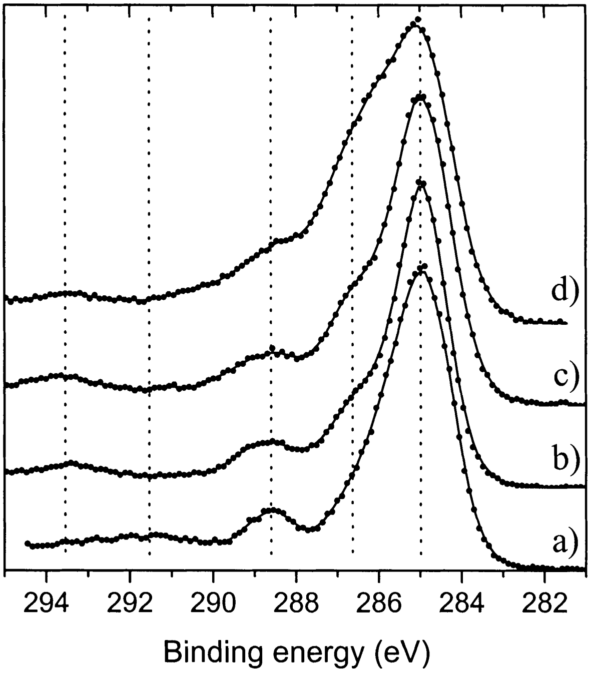


FIGURE 6 C 1s XPS spectra of PEI as a function of the plasma treatment time: (a) untreated PEI, (b) t = 60 s, (c) t = 150 s, (d) t = 600 s.

After 600 s plasma treatment, a small shoulder at 290 eV is even detectable, showing the formation of carbonate groups.

After treatment, the O 1s spectra (not shown) consist of a broad peak instead of two separate components as for degreased PEI, because numerous organic functions involving oxygen atoms are present at the surface. The N 1s spectrum is not much modified. No N-O bonds can be seen. A slight decrease of the binding energy from 400.7 eV to 400.3 eV is observed, which would be consistent with the formation of $O{=}C\text{-}NH_2$ or $\text{-}NH_2$ groups.

Figure 7 shows the valence band spectra of the same samples. A strong increase of the O 2s peak (not shown) confirms the oxidation of the surface. The spectrum of untreated PEI (sample a) is typical of polymers containing aromatic rings. The four components observed at 20.6, 17.3, 14.3, and 10.1 eV are a fingerprint of the aromatic backbone (mainly C 2s-type interactions) [15]. As shown in Figure 7, this curve shape is slightly modified after 60 s of treatment, much more after 150 s, and finally the valence band spectrum obtained after 600 s is completely different from degreased PEI. This result shows

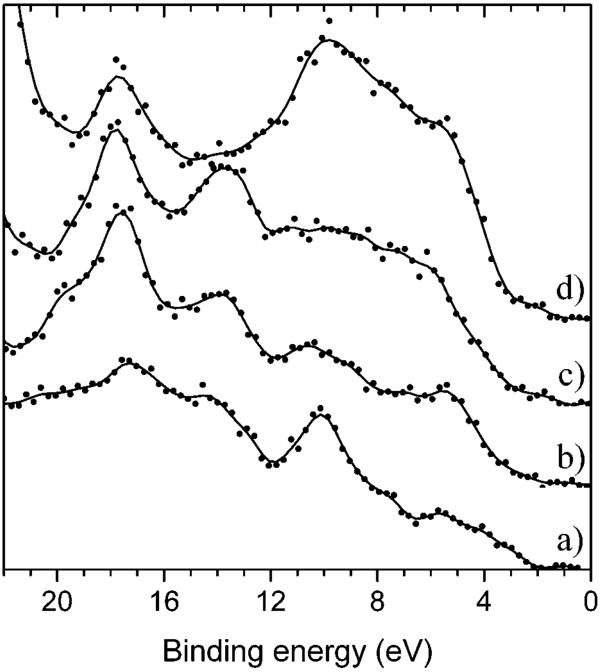


FIGURE 7 Valence band XPS spectra of PEI as a function of the plasma treatment time: (a) untreated PEI, (b) t = 60 s, (c) t = 150 s, (d) t = 600 s.

that plasma treatment induces numerous breaks of the C-C bonds, leading to the break of aromatic rings. This observation is in agreement with the shift of the C 1s satellite peak from 291.6 eV to 293.5 eV (Figure 6). Thus, cold plasma treatment of PEI surfaces leads to very strong chemical modifications involving C-C bond breaks and formation of C-O, C=O, and O=C-O bonds. Our results are in good agreement with previous works of Blackmann *et al.* [12] and Comyn *et al.* [16] concerning PEEK (increase of O/C ratio, creation of C-O, carbonyl C=O, and carboxylic acids HO-C=O) and of Asfardjani *et al.* [17] in the case of PEI (increase of the oxygen content at the surface by grafting of -OH groups, leading to HO-C=O and HOO-C=O groups).

In conclusion, the plasma treatment, in successive oxygen and argon discharges, causes a modification of the carbonaceous structure, an increase in oxygen content on the PEI surface (C-O and C=O bonds), and the probable appearance of ester or carboxylic functions. The formation of short oxidized mobile chains could occur, and the hygroscopic character of such species may induce the creation of unstable layers at the surface of the material [16].

Figure 8 shows the evolution of the contact angle between distilled water and freshly plasma activated PEI surface according to both treatment parameters (duration and power). For plasma power higher than or equal to 200 W, a rapid decrease of the contact angle (and thus an increase of the surface free energy) with treatment time is observed. This surface tension increase results simultaneously from the PEI surface functionalization by formation of C-O, C=O, and O=C-O bonds and carbon decontamination shown by the rapid increase of the O/C ratio in the interval (0;150 s) measured by XPS analyses.

Beyond 150 s of plasma treatment, the water contact angle stabilizes around 10–20°, according to the weak variations of oxygen and carbon concentrations of the PEI surface (Figure 9). For short processing times, the surface roughness changes weakly and the contact angle of water is directly sensitive to the oxidation state of the treated PEI surface. However, considering high power (800 W) or long irradiation time (600 s), wettability results, probably influenced by roughness, must be interpreted with care.

Plasma treatment does not systematically improve the adhesion properties of polyetherimide (Figure 10). On the one hand, the discharge at 600 W for 150 s increases the adherence with a change in

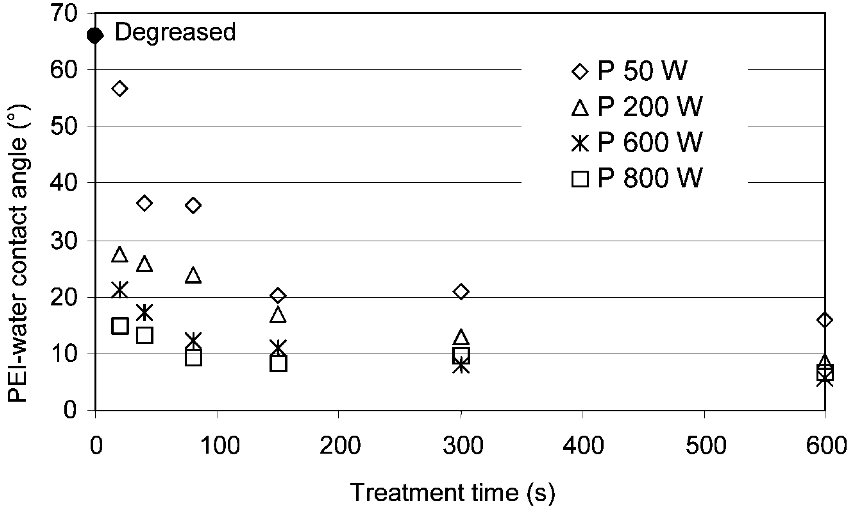


FIGURE 8 Variation of contact angle between PEI and distilled water according to both parameters of plasma: treatment time and power.

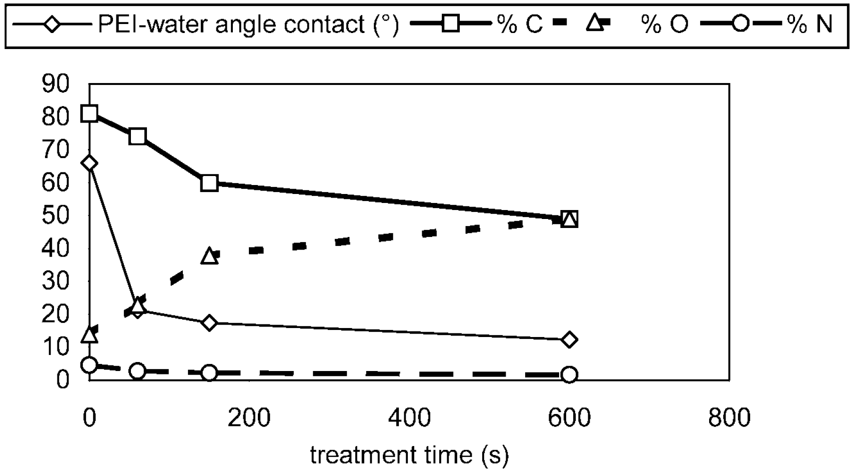


FIGURE 9 Variations of contact angle between PEI and distilled water, of the percentages of carbon, oxygen, and nitrogen at the PEI according to plasma: treatment time for 600 W power.

failure mode (interfacial to interfacial + cohesive) and a substantial increase (+25%) of the failure load. On the other hand, shear strength of single lap joints with PEI substrates pretreated at P (800 W, 150 s) or P (600 W, 600 s) falls drastically. Long time or high power activation,

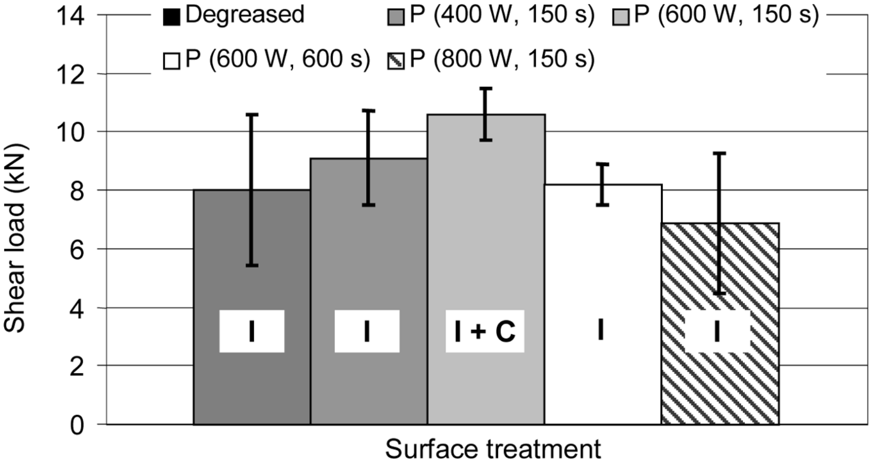


FIGURE 10. Joint shear strength and failure mode of samples following surface treatment: I, interfacial fracture; I + C, mixed (interfacial and cohesive) rupture.

involving an important exposure of the glass fibres at the surface, could thus become unacceptable for three reasons. The fibre, insufficiently fixed to the thermostable matrix, could be removed from the surface. This decohesion, if it takes place at the PEI/adhesive interface, can result in failure initiations. The loss of mechanical properties can also be the consequence of a poor adherence between glass fibres and epoxy adhesive. Another assumption is to consider a competition between oxidation and degradation of the PEI surface, consisting of short oxidised polymer chains unsuitable for a durable adhesion. Lastly, regarding the joint resistance in the hot/wet medium, the presence of fibres at the extreme surface can accelerate *via* capillarity water diffusion along the adhesive/PEI interface and thus favour a hydrolytic attack of joints.

Investigation of Bulk Adhesive Ageing

It is evoked, in the introduction, that the durability of adhesive bonded joints is considerably reduced under mechanical stress and in the presence of an aggressive medium associating heat and moisture. The hydrothermal degradation of joints then results either from a decrease of the mechanical properties of materials (generally those of the adhesive) or from a reduction of adhesion properties at the joint/sub-substrate interface, or even from both phenomena. This part deals with the consequences of the bulk adhesive ageing in the cooling liquid. Accordingly, mass uptake experiments due to liquid diffusion inside the adhesive were carried out, as well as thermomechanical analyses using rheometry. Thus, a sorption curve is shown in Figure 11 for the adhesive EA 9392 in the cooling liquid at 70°C.

Mass uptake (M_t%) is plotted *versus* the square root of time normalised to sample thickness ($\sqrt{t}/e$). At short times, the plot is a straight line passing through the origin. Afterwards, mass uptake reaches a pseudo equilibrium state, M_∞, around 5% (between 450 and 1750 h of immersion). Such features are comparable with Fickian type diffusion [18] where a liquid is considered as a single free phase driven within the polymer by the concentration gradient. Considering the linear part of the curve, a diffusion coefficient can be determined using the relation in Equation (2),

$$D = \frac{\pi s^2}{16 M_\infty^2}, \tag{2}$$

where s refers to the initial slope ($M_t/M_\infty < 0.6$). The diffusion coefficient, D_{70}, of a water–ethylene glycol mixture at 70°C within the adhesive was then evaluated to $1.56 \times 10^{-8} cm^2/s$. This value is

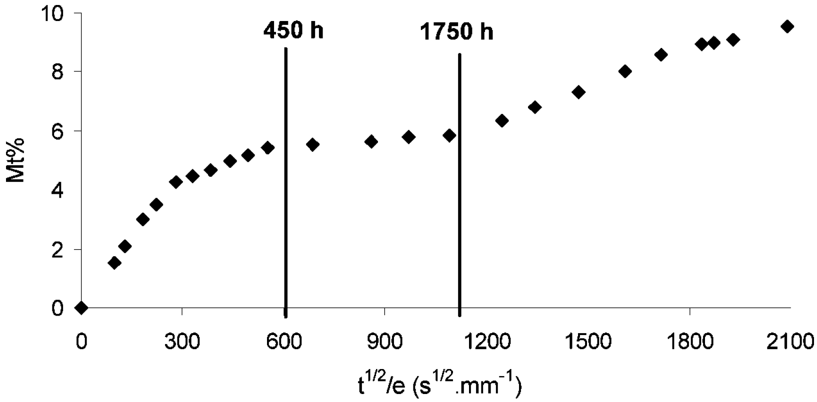


FIGURE 11 Relative mass uptake of the adhesive EA 9392 *versus* time of immersion in the ageing liquid at 70°C.

close to that found by De Nève and Shanahan [19] for an epoxy–amine network immersed in distilled water at 70°C.

For longer times (up to 1500 h) one observes an increase in the mass uptake that amounts to a positive deviation from the pseudoequilibrium, leading to a non-Fickian diffusion process. According to Crank [20], a time-dependent diffusion coefficient, after reaching the saturation level of the polymer, could be due to two simultaneous processes: structural changes within the polymer and a differential swelling between the surface and the sample core, which could induce network damage by irreversible expansions. This last phenomenon is predominant if the polymer contains fillers. Chateauminois *et al.* [21] previously reported a similar deviation, on the sorption curve, for a glass/epoxy composite immersed in water at 90°C and he attributed it, after a microscopic examination, to the creation of microcracks and voids within the matrix and at the matrix–fibre interface. The mass uptake thus becomes a measure that shows both water sorption within the epoxy–amine network and the filling of the hydrothermally created voids. On the other hand, the absorbed water during our ageing experiments is not totally removed after drying. The desorption process was carried out in the positive deviation with a liquid uptake M_t close to 8%. Residual mass is close to 6% after stabilization for samples desorbed in a desiccator and to 4% for samples air dried in an oven at 70°C. Zhou [22] proposed an explanation of residual water, invoking two kinds of bonded water. The first one, easily removed by desorption, is characterized by a single hydrogen bond between water molecules and the polymeric network. The second type involves the creation for a water molecule of more than one hydrogen bond *via* multiple interaction sites. In the latter case, a higher activation energy requires a high temperature for totally drying the sample.

Figure 12 gives desorption curves for previously aged specimens, for various immersion times in the cooling liquid (TGA analyses). A stabilization of the mass loss at 5% occurs around 210°C between 72 and 1440 h of ageing. This evolution confirms sorption kinetics of the adhesive presented in Figure 11, where the equilibrium state was reached between 450 and 1750 h. Secondly, for higher ageing times, desorption increases to 6.7% and 8.7% for samples aged for 2160 h and 4320 h, respectively, remembering again the positive deviation on the sorption curve. Furthermore, from 1440 h of ageing, a horizontal tangent, observed at 210°C, disappears progressively and the rate of mass loss increases strongly. To check possible damage to the adhesive, SEM observations of surfaces of an unaged and of a sample aged for 2160 h were performed. Figure 13a shows the initial surface of the adhesive sample where a few porosities and debris appear. The aged surface (Figure 13b) shows a totally damaged and "spongy" morphology, with numerous microcavities and a few microcracks. These observations partly confirm sorption behaviour (positive deviation of the curve after 1750 h of ageing) and desorption features (increase in the rate of weight loss); this was also noticed by Chateauminois *et al.* [21].

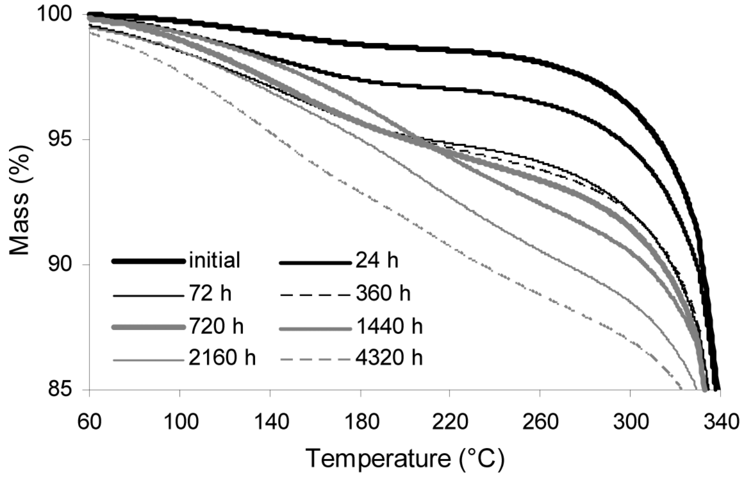
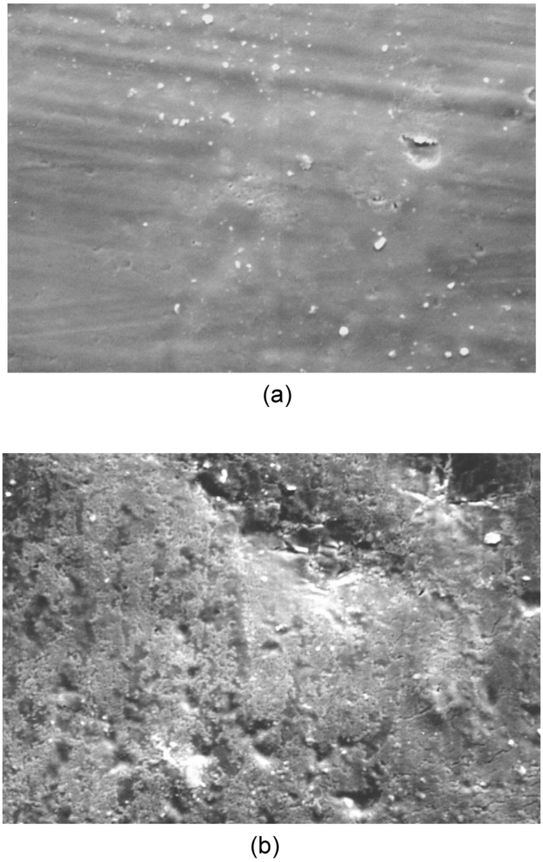


FIGURE 12 Thermogravimetric analysis curves of the adhesive EA 9392, according to various time of immersion in the ageing liquid at 70°C.



(a)

(b)

FIGURE 13 SEM micrographs (× 2500) of the adhesive EA 9392 surfaces: (a) unaged sample and (b) 2160 h-aged sample.

The influence of the ageing liquid's absorption on the thermomechanical properties of the adhesive was also evaluated using rheometry. Thus, the elastic modulus, G′, and the loss factor, tan δ, were measured with respective standard deviations equal to ± 5% and ±10%. Figures 14a and 14b show the variations of these two parameters as a function of temperature, for EA 9392 samples previously aged for 360 h on the one hand and 2160 h on the other hand in the ethylene glycol–water solution at 70°C, along with the same aged samples that were also subjected to air drying in an oven at 70°C. In the latter case, the time of drying was sufficiently long to reach the mass stabilization. The aim of this drying was to observe the possible reversibility of the liquid medium uptake by the adhesive.

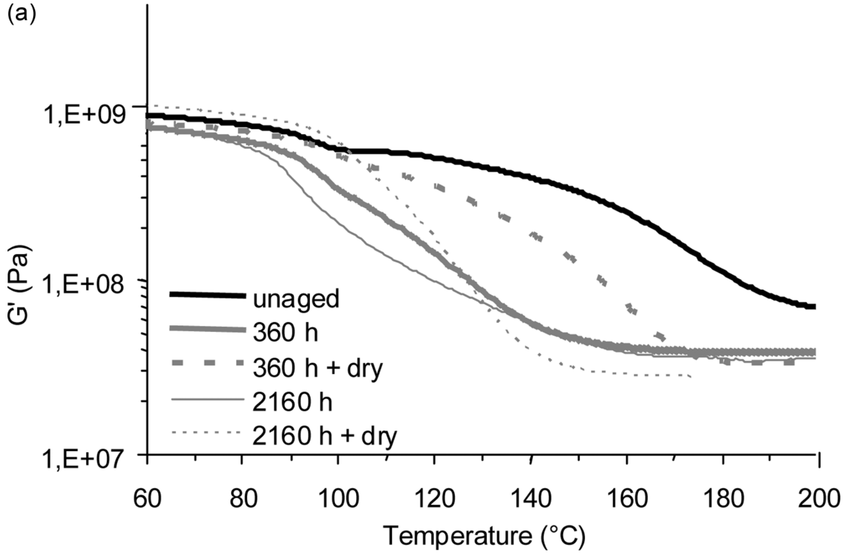


FIGURE 14 (a) Elastic modulus (G′) of the adhesive EA 9392 *versus* temperature at different stages of ageing in the ethylene glycol−water solution at 70°C.

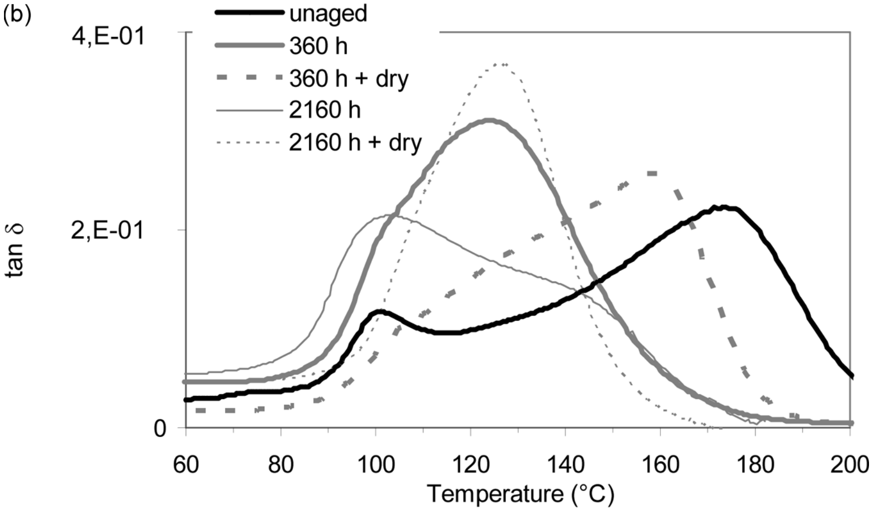


FIGURE 14 (b) Loss factor (tan delta) of the adhesive EA 9392 *versus* temperature at different stage of ageing in the ethylene glycol−water solution at 70°C.

On the other hand, the tan δ-temperature plot allows the determination of the alpha relaxation temperature (T_{α}) of a polymer. It is noteworthy that T_{α} values are measured at the maximum of tan δ curve (horizontal inflexion point). However, if the $T_{\alpha 1}$ is partly hidden by the $T_{\alpha 2}$ one, $T_{\alpha 1}$ (close to 101°C) is measured at the point of positive derivative of the curve. Two values of the alpha relaxation temperature, $T_{\alpha 1}(101 \pm 2^{\circ}C)$ and $T_{\alpha 2}(173 \pm 2^{\circ}C)$, corresponding to the rheological appearance of two glass transition temperatures, are evidenced in Figure 14b for the unaged sample. These two temperatures result from an optimal polymerization procedure of the adhesive (4 h at 80°C), with a cure energy close to 325 J/g (DSC measurements). Thus, according to stoichiometric calculations and literature data for epoxy/amine networks [23], the $T_{\alpha 1}$ is linked to the DGEBA-EDA network of the adhesive and $T_{\alpha 2}$ to the TGDMA-BAPP one.

Concerning the adhesive elastic modulus, G', it is interesting to divide the G'-temperature plots into three intervals: $T < T_{\alpha 1}$, $T_{\alpha 1} < T < T_{\alpha 2}$, and $T > T_{\alpha 2}$, knowing here that G' is the glassy elastic modulus (G'_g) for $T < T_{\alpha 1}$ and is the rubbery elastic modulus (G'_r) for $T > T_{\alpha 2}$ (Figure 14a). At 70°C, the G'_g decrease is 16% for an ageing time of 360 h and 19% for 2160 h. The glassy modulus, however, recovers its initial value after drying. Such a reversibility is consistent with the adhesive plasticization by the ageing liquid. On the other hand, it is noteworthy that the initial rubbery modulus, G'_r (70 MPa), falls to 39 MPa at 360 h of ageing and tends towards the constant value of 35 MPa (maintained after drying) from 2160 h. The G'_r decrease goes also with a broadening of the tan δ corresponding to the TGDDM-BAPP network, along with a shift of $T_{\alpha 2}$ towards a lower temperature (with a partial recovery after drying) while $T_{\alpha 1}$, corresponding to the DGEBA-EDA network, remains constant (Figure 14b).

Figure 15 collects these results and shows the variations of G'_g, G'_r, $T_{\alpha 1}$ and $T_{\alpha 2}$ *versus* mass uptake, for different times of ageing (0 h, 360 h, 720 h, 1440 h, 2160 h, and 4320 h) of EA 9392 in the ethylene glycol–water solution.

The previous observations are corroborated and the decreases of G'_g and G'_r are well linked to the mass uptake. The most remarkable effect concerns the linear decay of $T_{\alpha 2}$ associated with the TGDDM-BAPP network, with a loss of 50°C at 360 h of ageing. One percent of mass uptake yields a loss of 9°C for $T_{\alpha 2}$, while $T_{\alpha 1}$ is little influenced by the liquid absorption. Thus, if there is a plasticization of the adhesive by the ageing liquid at 70°C, this phenomenon is mainly due to a strong modification of the TGDDM-BAPP network.

To confirm this hypothesis, experiments were carried out in the same conditions of ageing for a TGDDM-BAPP system alone. The

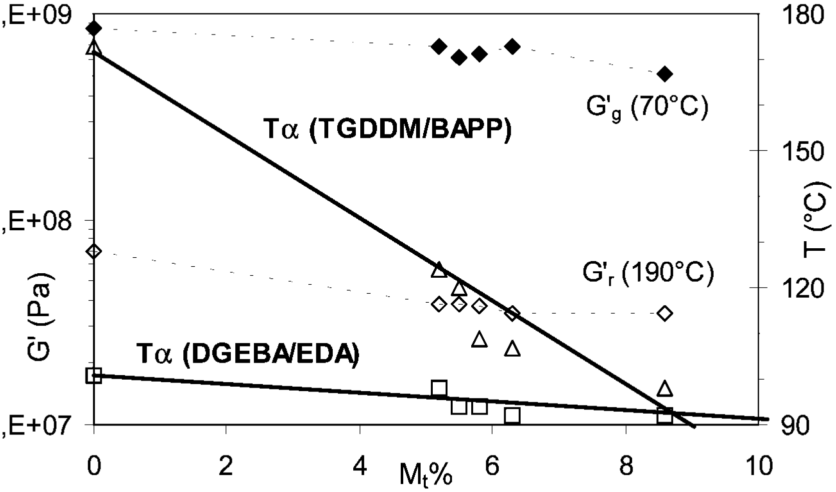


FIGURE 15 Glassy modulus at 70°C (G'_g), rubbery modulus at 190°C (G'_r) and α relaxation temperatures associated to DGEBA-EDA ($T_{\alpha 1}$) and TGDDM-BAPP ($T_{\alpha 2}$) networks of EA 9392 adhesive, *versus* mass uptake ($M_{t\%}$).

TGDDM resin was MY720 from Dow Chemical (Dow France, Paris, France). According to the relation in Equation (2), the coefficient, D_{70}, for the diffusion of the ethylene glycol–water mixture at 70°C within the TGDDM-BAPP system is equal to $1.41 \times 10^{-8}\,cm^2/s$, a value close to that measured by Nogueira *et al.* ($1.39 \times 10^{-8}\,cm^2/s$) [24] and by Zhou and Lucas ($1.15 \times 10^{-8}\,cm^2/s$) [25], on epoxy systems containing TGDDM and aged in water at 70°C and 75°C, respectively. These authors also mentioned the decrease of the α relaxation temperature close to 34°C for a TGDDM/DDS sample which was simply aged for 10 h in water at 100°C. For the same epoxy system, Zhou and Lucas [25] displayed a T_α collapse close to 140°C after an immersion in water at 60°C for two months (1500 h). Comparatively, for an EA 9392 sample immersed in our ageing liquid for the same time, the $T_{\alpha 2}$ decrease is about 60°C.

To summarize, all of these results support the deleterious effect and the strong interaction between the TGDDM-BAPP system of EA 9392 adhesive and our ethylene glycol–water solution. There is a plasticisation of the adhesive by the liquid, and this phenomenon causes a strong and irreversible decrease of the rubbery modulus of the adhesive at high temperatures (over 180°C). At 70°C and for ageing times less than 2160 h the plasticization is reversible and weakly influences the mechanical properties of the bulk adhesive. The latter observation must be taken into account for the following study.

Durability Study of the -PEI/Epoxy Adhesive-Interface

Shear tests by compressive loading were carried out during the ageing campaign.

The surfaces of aged samples showed interfacial failures after shear testing with higher rupture loads for the plasma-treated samples (600 W; 150 s). No significant change in failure load values appears for degreased samples whatever the ageing time (Figure 16). However, concerning plasma-treated samples, the loss of mechanical properties is close to 20% between unaged and aged samples and remains constant according to ageing time. Note that this type of test is less severe (the adhesive joints were not stressed during ageing) than the wedge test.

In this work, the tough asymmetric wedge test was the main investigation tool for the accelerated degradation of the PEI/adhesive interfaces in our aggressive medium. Using Xiao abacuses [9], phase angle, which represented the ratio between shear and normal stresses at the interface near the crack tip, was about $-12°$. The shear/cleavage ratio was equal to 0.2, and thus loading at the crack tip was close to a pure normal stress.

Four major key points are highlighted from cleavage test examinations. The first point is the *crack localization*, which in our case was

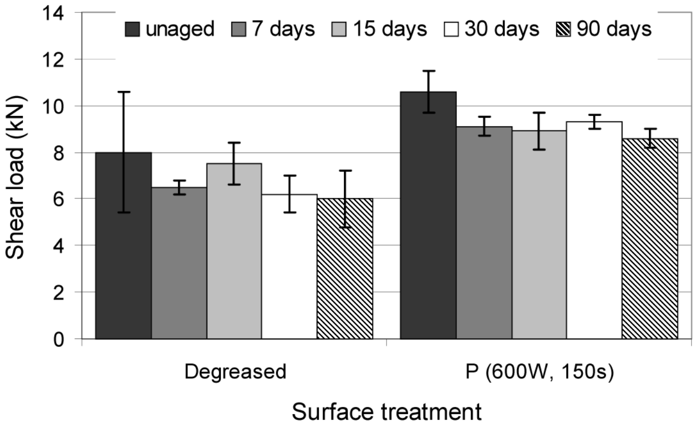


FIGURE 16 Compression shear failure loads for 5 ageing times in the cooling liquid at 70°C and for two different surface treatments of PEI substrates.

always visually interfacial. The second point is the *crack length*, before the immersion in the aggressive medium, which results from the load required for breaking polymer fibres one by one or for breaking substrate–adhesive interfacial bonds, is the expression of the initial adherence or of the polymeric adhesive's cohesion. The third point is the initial slope or the *crack speed*, which is symptomatic of the resistance of substrate–adhesive interfacial bonds in the cooling liquid. This resistance varies according to the nature of bonds set up at the interface. The fourth point is the *stabilization (or not) of the crack lengths*, according to ageing time, which is characteristic of a tolerance threshold to the applied stress and of the nature of interfacial bonds. In other words, whatever be the applied load, if the crack length increases with time until it reaches the bottom of the bonded assembly, this means that there is no maximal applied load (or tolerance threshold) corresponding to the crack stabilization. Such a case evidences weak interfacial bonds and, on the opposite, a crack stabilization corresponds to stronger interfacial bonds.

So, the initial crack length varies from 17.4 mm for bonded assemblies made with degreased PEI substrates to 12.0 mm when substrates are plasma treated (Figure 17). The corresponding fracture energies are 200 J/m^2 and 775 J/m^2, respectively. The improvement factor of adhesion properties is then equal to 3.8, after plasma treatment. However, after a simple degreasing, bonding PEI is effective, probably because of an interdiffusion, in amorphous areas, of monomers chains

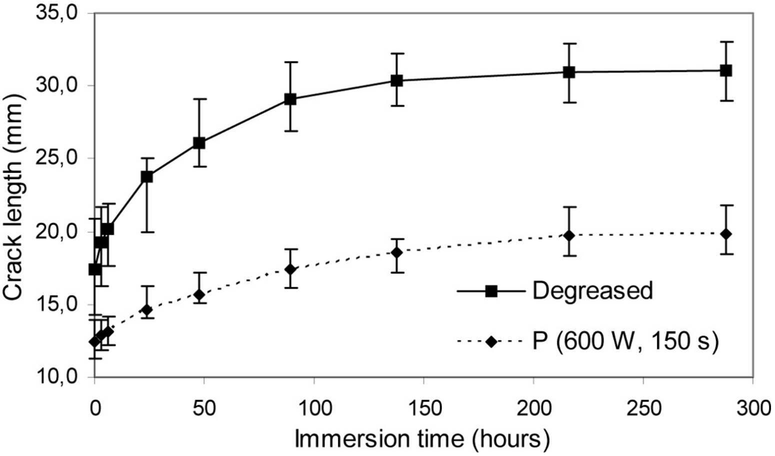


FIGURE 17 Crack lengths (asymmetric wedge test) versus immersion time in the cooling liquid at 70°C, for two different surface treatments of PEI substrates.

during curing. On the other hand, crack speeds at PEI/adhesive interface for degreased and plasma-treated substrates are 0.17 µm/s and 0.04 µm/s, respectively. The creation of strong bonds at plasma-treated PEI/adhesive interface could be considered, as normal stresses at the crack tip are higher (the crack length is comparatively lower). Thus, the interfacial degradation of plasma-treated PEI/EA 9392 joints are considerably reduced in the ageing liquid at 70°C.

Concerning the crack length variations *versus* ageing time (Figure 17), a great dispersion of results is observed for the joints with degreased substrates. However, both curves show a stabilization of the crack length, or a tolerance threshold to the applied stress, after 150 h of ageing. The difference between crack lengths prior to and after ageing is consistent and results in a loss of fracture energy of 80% for simply degreased PEI substrates and of 67% for plasma-treated ones against a loss of mechanical properties in the shearing mode, for plasma pretreated surfaces, close to 20% after three months of humid ageing (Figure 16).

The latter result is in agreement with bulk adhesive characterizations (§ 3.2), which show little modification of mechanical properties of the aged adhesive in spite of the plasticizing effect of the ageing liquid at 70°C. Zanni-Desfarges and Shanahan [26] have shown, on a similar adhesive system, a loss of mechanical properties of structural adhesive joints much faster than the one noted for the bulk adhesive alone. In our case and in an opposite way, an important molecular anchoring of the DGEBA-EDA network at the PEI/adhesive interface is very likely restricting the joint degradation in the cooling liquid at 70°C.

CONCLUSIONS

From a technological and scientific point of view, the work described in this article presents information concerning the durability of structural adhesive joints in a hot/wet medium through, in particular, a multifield approach based on surface, bulk adhesive, and joint characterizations.

- This study reveals that cold plasma treatment is an effective tool to optimize adhesion between polyetherimide substrates and an epoxy adhesive. Appearance of microroughness and new polar functions, along with a reduction of contaminants at the PEI surface, constitute the potential causes of the adherence improvement. However, for too much treatment duration or power, a degraded surface with an exposure of glass fibres induces a loss of mechanical properties of joints.

- The inherent constraints associated with manufacturing and in-service functioning of converters force the adhesive to have specific physicochemical properties (flexibility, thermal, and chemical resistance). A structural epoxy adhesive (EA 9392) made up of two polymeric epoxy/amine networks (DGEBA-EDA and TGDDM-BAPP) and containing an elastomeric phase has been studied. Mass uptake measurements *versus* time showed two different processes for the liquid diffusion in the bulk adhesive, a pseudo-Fickian first stage until an equilibrium state, and a non-Fickian second stage for longer times associated with microscopic damage of the adhesive. Ageing of the bulk adhesive in an ethylene glycol–water solution at 70°C lies in its plasticization with a degradation of one of its two polymer networks (TGDDM-BAPP). The consequence is a strong and irreversible decrease of the adhesives rubbery modulus (for $T > T_{\alpha 2}$) and of the α-relaxation temperature ($T_{\alpha 2}$) of the TGDDM-BAPP network, while the glassy modulus endures well despite microcracks within the adhesive aged 2160 h. This dissimilar mechanical behaviour of the adhesive, according to temperature, can be explained by the different parts played by the two polymer networks. Indeed, the TGDDM-BAPP network, designed for high temperatures, is strongly damaged while the DGEBA-EDA network resists well the aggressive ethylene glycol–water solution at 70°C.
- Mechanical tests of adhesive bonded joints, according to two failure modes (shearing and cleavage), have been used to characterize the degradation of PEI/adhesive interfaces in the ethylene glycol–-water solution at 70°C. Bonding PEI with a structural epoxy adhesive appears to be an efficient assembling technique. Rupture shear strengths of 34 ± 3 MPa are reached with cold-plasma–-treated PEI assemblies. Such a value is seven times as high as the one required for this power integration application and remains sufficient after ageing (25 ± 3 MPa) (a loss close to 20%). The asymmetric wedge test clearly shows the considerable resistance of joints with cold-plasma–treated PEI substrates (fracture energy $G = 250\,J/m^2$) compared with only degreased ones ($G = 40\,J/m^2$). Moreover, the suitable behaviour of bonded assemblies during ageing is, thus, in agreement with the bulk adhesive stability at 70°C in the cooling liquid. However, new experiments on both bulk adhesive and bonded joints for longer ageing times will be needed to ascertain the DGEBA-EDA network's long-term durability along with better identification of the influence of microcracks on adhesive mechanical properties. In these conditions, rheometry and

mechanical rupture tests appear clearly to be complementary techniques for the study of bonded joint durability.

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