

Preadhesion treatment of thermoplastic adherends using excimer laser

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Preadhesion treatment of two thermoplastic substrates (Lexan polycarbonate and Ultem polyetherimide) by means of ArF excimer laser has been evaluated by comparing the lap shear strengths of polyurethane-bonded joints with untreated, laser-treated and SiC abraded adherends. Experimental results showed a significant increase in lap shear strength following ArF laser treatment. Different laser conditions were needed to achieve the same level of bond strength improvement for both thermoplastic adherends. Surface analysis of the ArF laser-treated adherends and the fractured polyurethane joints revealed morphological and chemical modifications due to the intense ultra-violet laser irradiation. For best results laser irradiation intensity, dose and operating atmosphere should be further studied.

Key words: adhesion; surface treatment; excimer laser; surface morphology; surface chemistry; polycarbonate; polyetherimide

In recent years, the intensified development of ultra-violet (UV) laser systems has led to an increasing tendency to use these devices in various process applications. The main uses include cleaning of surfaces, precise cutting of materials, photopolymerization, ablation, coating in microelectronic circuits and surgical applications. The outstanding feature of UV laser radiation is its ability to break chemical bonds or cause chemical reactions on the radiated surface due to photochemical effects in addition to a thermal heating effect. The range of wavelengths of UV lasers is within the energy of almost all organic chemical bonds. The ability to use specific coherent energies can result in specific chemical reactions which are otherwise difficult to obtain. The change of wavelength can also determine the amount of heat effect compared with photochemical effect.

Present processes for prebond surface preparation of thermoplastic adherends involve the use of abrasive, chemical and plasma treatments, which are to a certain extent destructive, poorly controlled and introduce undesirable changes in the morphology and composition of the surface such as cracks, uncontrolled pitting and contamination. In a previous paper¹, the potential of using infra-red (IR) and UV lasers for prebonding surface treatments of polyetherimide (Ultem) and polycarbonate (Lexan) substrates was demonstrated. Laser treatment provided a clean and

rather simple method of surface preparation and reduced the extent of damage to the treated surfaces. The UV laser proved to be the most effective treatment (compared with continuous and pulsed IR lasers) due to its specific mechanism which involves chemical activation with minor heat effects. In the present investigation, the application of ArF excimer laser (UV laser) for surface treatment of the thermoplastic adherends (Ultem and Lexan) prior to adhesion is further evaluated and studied.

Experimental

Laser treatment

The laser used during the course of this investigation was an excimer laser 201 MSC, a product of Lamda Physik, FRG, with the following parameters: repetition rate of 10 Hz; intensity 110 mJ/pulse; beam density of 83 mJ/pulse/cm²; and area of 22 × 6 mm. Number of pulses ranged between 1 and 200.

All experiments were conducted at ambient temperature and in an air environment.

Adherends, adhesive and testing

Two adherends were used: Lexan 9023-112 polycarbonate (from General Electric) and Ultem 1000 polyetherimide (also from General Electric). The

surfaces of the laser-treated and untreated adherends were studied for chemical changes due to irradiation by electron spectroscopy for chemical analysis (ESCA). A model PHI 555 spectrometer was used, with an Al $K\alpha$ X-ray source, at 10 kV, 40 mA and pressure of 3×10^{-8} torr.

Laser-treated adherends were bonded by means of a two-component polyurethane adhesive (Hexcel, USA), joints being prepared four days after the laser treatment which proved to be the optimal 'open time'¹. Joint properties were determined using single lap shear (SLS) tests according to ASTM D-1002-72. Specimens were tested 10 days after preparation in an Instron machine, model 1185, at a rate of 20 mm min⁻¹. The mode of failure was determined visually to be either adhesive (interfacial — 100% coverage of adherends) or cohesive (200% coverage of adherends). Fracture surface morphology was analysed by means of scanning electron microscopy (SEM) using a model JSM-840 instrument from Jeol, Japan. Fracture surfaces were Au/Pd sputtered prior to analysis. Chemical changes due to laser treatment at the fracture surface were investigated by means of Fourier transform infrared spectroscopy (FTIR) using a Nicolet 5XD spectrophotometer in an external specular mode, equipped with a horizontal stage in a near-to-normal incidence and a gold-coated mirror as reference.

Two types of reference were used for each set of experiments, one in which adherends were untreated and another where adherends were abraded with SiC (36 mesh). The level of adhesion was determined relative to the SLS strength of SiC-treated adherends.

Results and discussion

Fig. 1 presents the SLS strengths of polyurethane-bonded joints with untreated adherends and with laser-treated adherends as a function of the number of laser pulses. The ArF excimer treatment seems to be very effective on both adherends, with the laser-treated polycarbonate and polyetherimide achieving lap shear strengths up to 60% higher than their SiC-abraded counterparts. However, a distinct difference can be seen in the behaviour of the two substrates. While the polycarbonate reaches an optimal adhesion strength value after about 12 pulses, the polyetherimide adhesion improves gradually as more pulses are

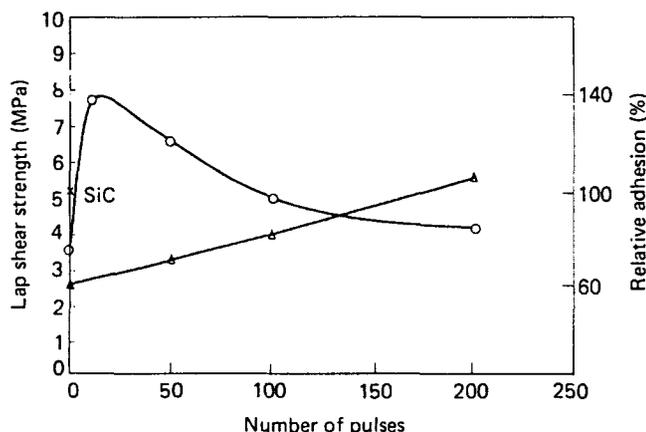


Fig. 1 Single lap shear strengths of polycarbonate (O) and polyetherimide (Δ) adherends treated with excimer laser (X, value for both adherends treated with SiC)

applied (up to 200 pulses). Even then no equilibrium is reached, although mild deterioration of the surface can be detected visually.

The excimer laser emits at a wavelength of 193 nm, an energy high enough to break nearly all chemical bonds, ejecting atomic and molecular fragments from the surface at supersonic velocities. This mechanism is ablative photodecomposition. Thus, excimer laser energy changes the chemical composition and the nature of the surface. These results confirm the conclusions drawn in the previous work¹, and indicate that the same trend and behaviour continues at higher energy treatments.

SEM micrographs of polycarbonate treated with UV laser reveal morphological changes exhibited as conic, rounded granules spread all over the surface (Fig. 2). The more energy supplied by the laser (i.e., the greater the number of pulses), the denser is the concentration of the granules on the surface and the smaller their size becomes. Figs 3(a)–3(d) show how the number of laser pulses affects the adherend layer morphology and its replica on the adhesive layer. It can be seen that the surface of the adhesive shows a better replica of the granules at more energetic treatments. At 100 pulses, and even more pronounced at 200 pulses, a weakening of the treated layer of the adherend is observed (ablation) and the granules are plucked off the polycarbonate surface by the adhesive at failure (the failure mode being partly cohesive failure in the adherend), see Figs 4(a) and 4(b). However, the enhanced adhesion due to mechanical interlocking is clearly revealed in Fig. 5 at 10 pulses treatment, and at all UV laser treatments adhesive can be found on each adherend, showing far better adhesion than for the untreated adherend (Figs 6(a) and 6(b)). Thus the ablation phenomenon at higher energies and the intense adhesive locking following treatment of the adherend for 10 laser pulses explain the optimum adhesion strength at about 10 pulses of UV laser treatment for the polycarbonate adherend.

SEM micrographs of polyetherimide treated with excimer laser also show morphological changes exhibited as granules spread all over the surface (Figs 7(a) and 7(b)). The adherend layer morphology and its replica at the adhesive layer shows that the more energetic the treatment, the larger the granules appear (Figs 8(a)–8(c)) and the more concentrated in groups they

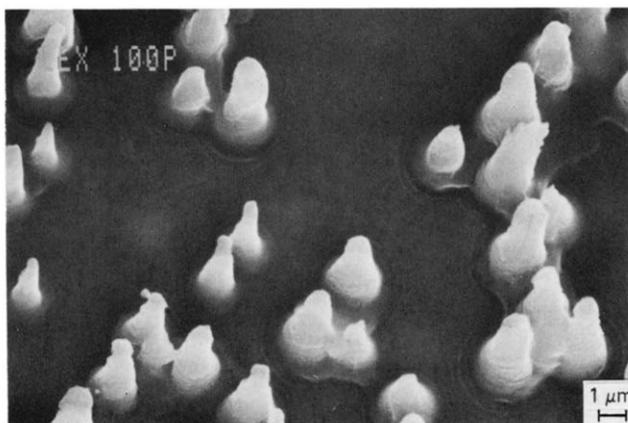


Fig. 2 SEM micrograph of polycarbonate treated with excimer laser (100 pulses)

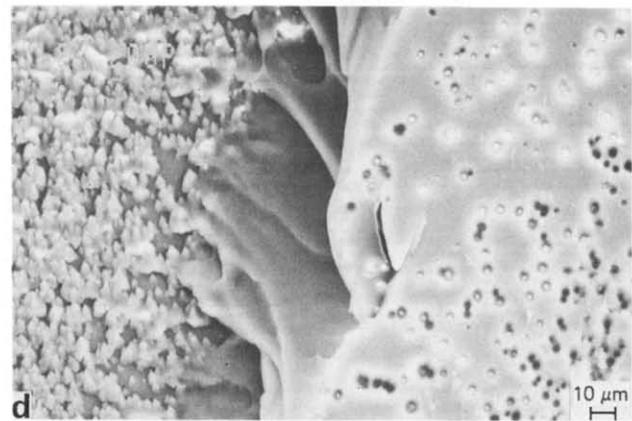
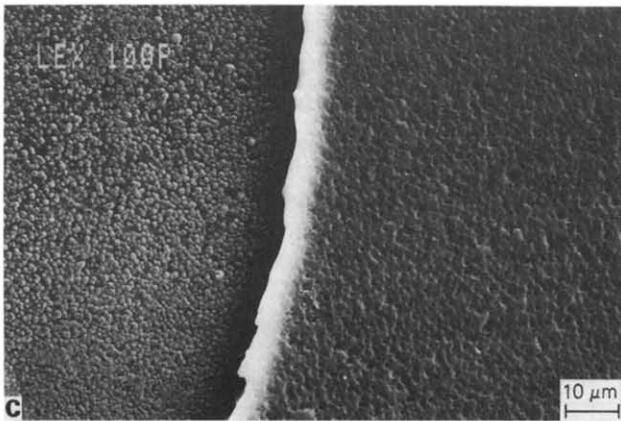
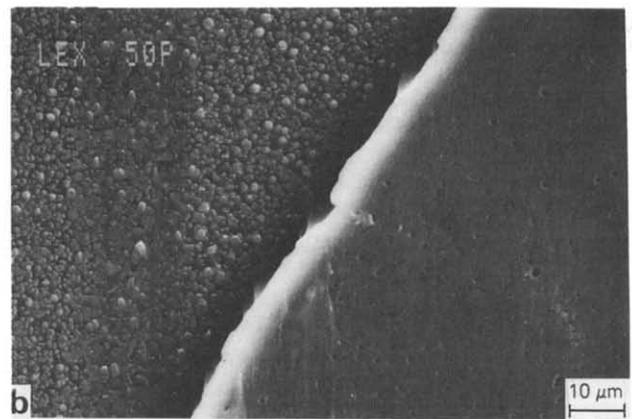
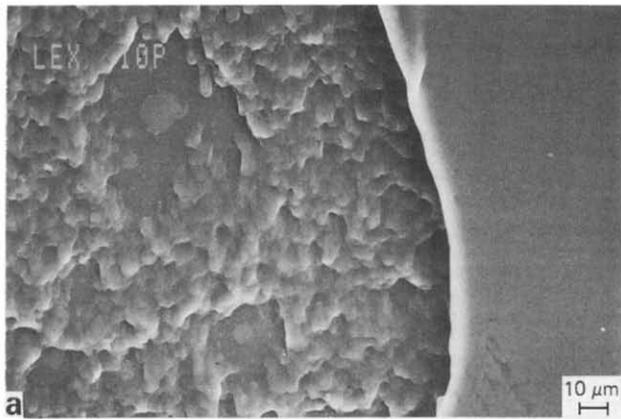


Fig. 3 SEM micrographs of cohesive fractured joint surfaces of polyurethane-polycarbonate treated with excimer laser radiation: (a) 10 pulses; (b) 50 pulses; (c) 100 pulses; (d) 200 pulses

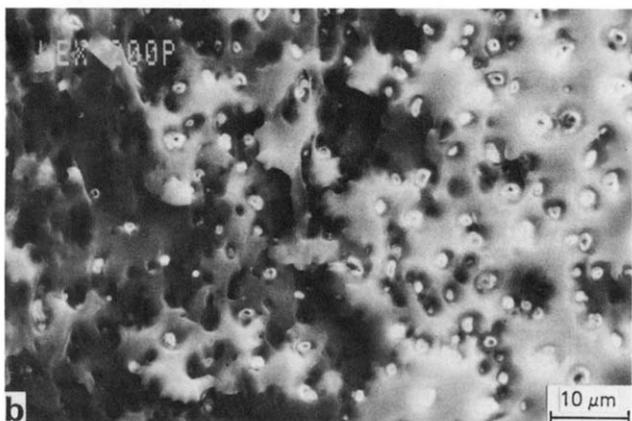
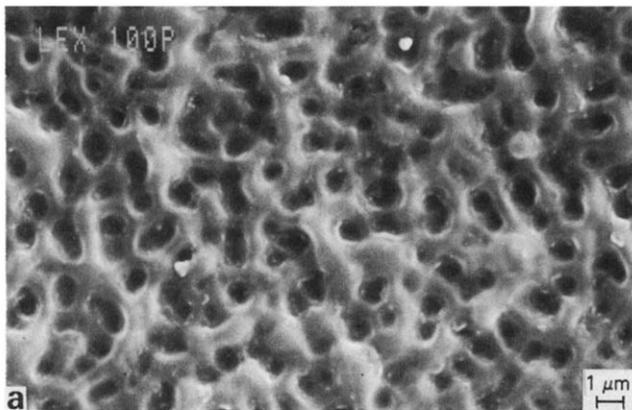


Fig. 4 SEM micrographs of cohesive fractured joint surfaces (adhesive side) of polyurethane-polycarbonate treated with excimer laser: (a) 100 pulses; (b) 200 pulses

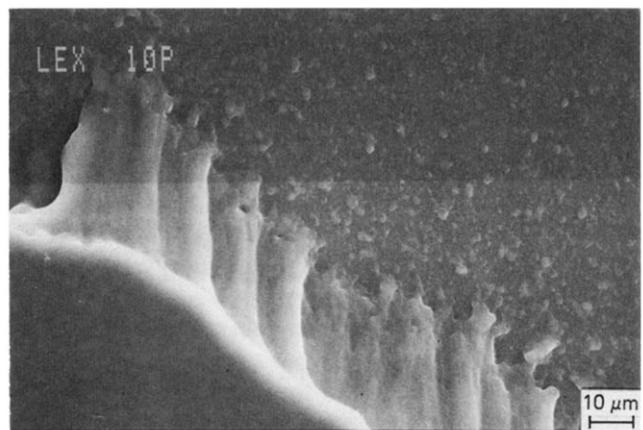


Fig. 5 SEM micrograph of fractured joint surfaces of polyurethane-polycarbonate treated with 10 pulses of excimer laser

become (Fig. 7(b)). The surface of the adhesive shows a better and deeper replica of the granules at more energetic treatments and no ablation is observed (Figs 9(a) and 9(b)). The interlocking improves at longer treatments, which explains the increase of adhesion strength of polyetherimide with treatment time and energy.

In addition to the pronounced morphological modification, chemical changes also take place following UV laser treatment of the adherends. Table 1 summarizes these changes depicted by FTIR. It is evident that an increase in surface polarity of the polycarbonate occurs due to the scissioning of carbonate bonds to form hydroxyls and carboxyls as shown in the following scheme²⁷:

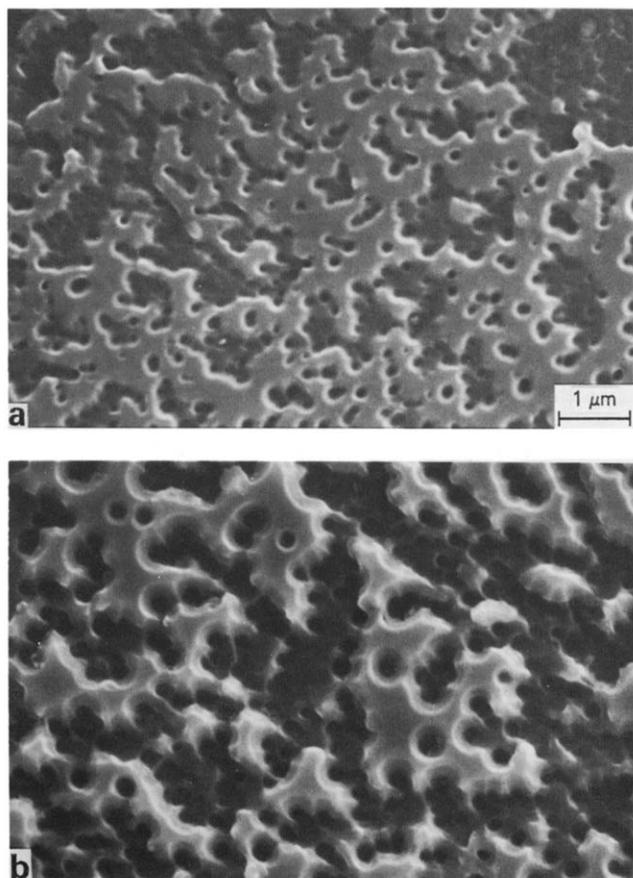


Fig. 9 SEM micrographs of fractured joint surfaces (adhesive side) of polyurethane-polyetherimide treated with excimer laser radiation: (a) 100 pulses; (b) 200 pulses

polycarbonate. Changes occur mainly at the imide ring, to form polyamic acid, which improves the surface chemical activity^{3,4}.

ESCA analysis was performed on untreated adherends and on adherends after 12 laser pulses (polycarbonate) and 200 laser pulses (polyetherimide), and revealed the amounts of oxygen, nitrogen, carbon

and contaminant at the surface of the untreated and treated adherends. As can be clearly seen in Figs 10(a), 10(b), 11(a) and 11(b), laser treatment evaporates the contaminants (Si, Ca, Na and N) from the adherend

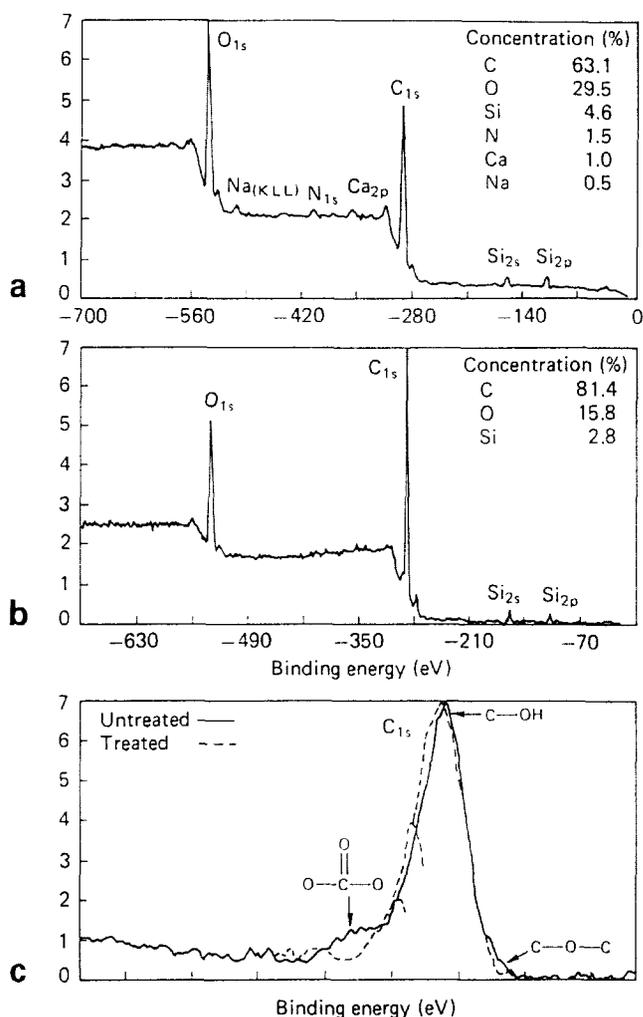


Fig. 10 ESCA spectra of polycarbonate (a) before and (b) after laser irradiation and (c) a comparison spectrum of C_{1s}

Table 1. FTIR normalized absorption* of polycarbonate and polyetherimide adherends (before and after UV laser treatment)

Adherend	Absorption wavenumber (cm ⁻¹)	Assignment of chemical group	Normalized absorption		
			Number of pulses		
			0	50	200
Polycarbonate	1794	C=O bound	0.63	0.54	0.50
	1544, 856	COOH	0.40	0.45	0.68
	1362	COO	1.03	1.26	1.18
	1294	φCO	0.73	0.67	0.61
	1206	COOH (hydrogen bonded)	1.12	1.23	1.50
	784	φ (aromatic)	0.54	0.32	0.26
Polyetherimide	1780	Open imide	0.75	-	0.93
	1740, 750	Closed imide	1.0, 0.6	-	0.9, 0.57
	1280	φCN	0.70	-	1.00
	1634	CO-NH ₂	0.75	-	0.48
	1625	C=O free	0.80	-	0.87
	1423	C-C(OH)-C	0.72	-	0.84
	750	Imide (aliphatic)	0.60	-	0.57

*Relative absorption normalized to 1515 cm⁻¹ (aromatic)

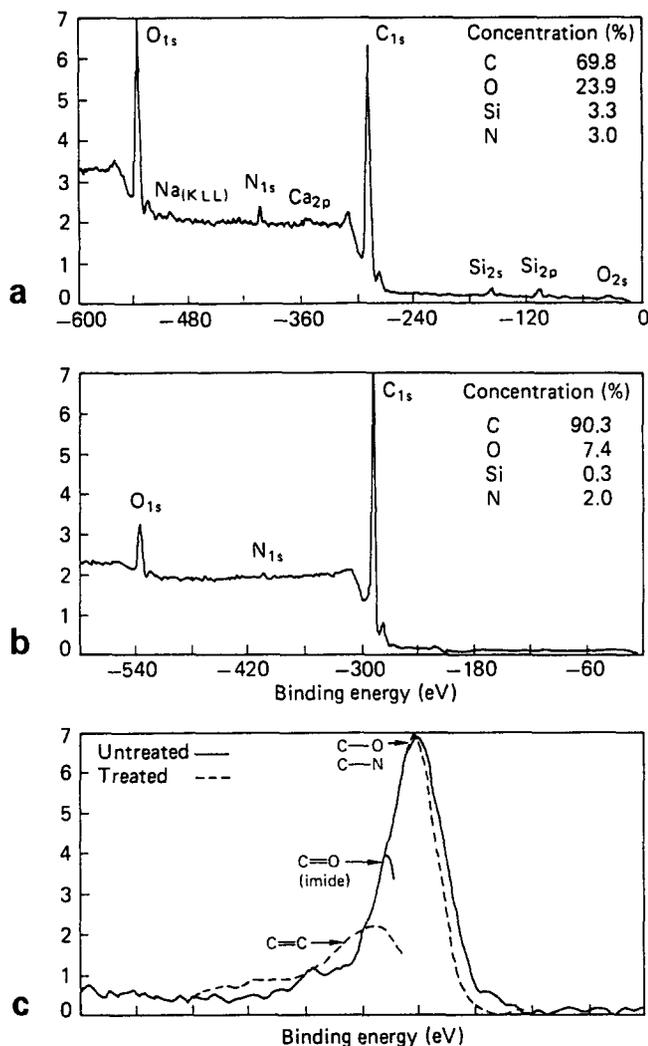


Fig. 11 ESCA spectra of polyetherimide (a) before and (b) after laser irradiation and (c) a comparison spectrum of C_{1s}

surface, leaving it cleaner. The ratio of O/C in the polycarbonate and O/C and N/C in the polyetherimide decreased drastically following laser irradiation (by 53–75%), probably due to decomposition.

The C_{1s} spectrum of both adherends changed as a result of the laser treatment (Figs 10(c) and 11(c)). In the treated polycarbonate, the C_{1s} spectrum showed a decrease in the peak at 290.9 eV assigned to the carbonate group (O-C(=O)-O) and an increase in the peak at 288.5 eV corresponding to hydroxyl (C-OH) or carboxyl (C=O)⁵ functional groups, indicating the formation of esters and alcohols deriving from chain scission of the carbonate groups. The new chemical groups are more reactive towards the polyurethane's functional groups than the carbonates, and thus may improve the adhesion level.

In the treated polyetherimide, the C_{1s} spectrum shows a decrease in the peak at 288.5 eV assigned to the carbonyl group of the imide ring and an increase in the 286.4 eV peak corresponding to carbon atoms bonded to oxygen and nitrogen. This change indicates that the imide ring is the group mainly affected by laser irradiation, confirming the FTIR results (Table 1). Active groups such as esters and amides are probably formed during the emission of CO, CN and HCN fragments⁶, thus creating an active surface with better adhesion capability.

Conclusions

The use of ArF excimer laser as a preadhesion surface treatment for two thermoplastic substrates, polycarbonate and polyetherimide, has been investigated. Polyurethane-bonded joints made with treated adherends had higher lap shear strengths than joints with untreated adherends. Scanning electron microscopy revealed morphology changes and infra-red and ESCA spectroscopy indicated chemical modifications to the surface of both substrates following laser treatment. Under optimal excimer treatment the mode of failure became cohesive in nature. Increased surface roughness and the introduction of more active chemical groups on the surface of the treated adherends are both responsible for the higher adhesion joint strength. It is difficult to indicate which mechanism contributes more to the increased joint strength since both effects occur together during the UV laser treatment.

The thermal properties and chemical composition of the thermoplastics are the decisive factors affecting their final adhesion. Polycarbonate, with its lower T_g and more sensitive skeletal chain structure, becomes activated by low energy treatment of the UV laser and shows marked signs of ablation at high energy treatment. On the other hand, polyetherimide, with its higher T_g and more inert chemical structure, becomes activated only at very energetic treatment with the UV laser and shows minor chemical signs of degradation.

The thorough morphological analysis by SEM and chemical analysis by FTIR and ESCA not only indicated the success of the preadhesion treatment by UV laser, found in the authors' previous work¹, but also enabled the understanding of the phenomena observed in the mechanical tests.

It can be concluded from the present study that ArF excimer laser is an effective, clean and accurate method for surface preadhesion treatment of polycarbonate and polyetherimide, compared with conventional abrasion methods. For best results laser irradiation intensity, dose and operating atmospheres should be studied for each polymer.

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