

Wettability characteristics of polyethylene modified with CO₂, Nd:YAG, excimer and high-power diode lasers

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Abstract: Interaction of CO₂, Nd:YAG, excimer and high-power diode laser (HPDL) radiation with the surface of the biomaterial polyethylene (PE), was found to effect varying degrees of change to the wettability characteristics of the material depending upon the laser used. It was observed that interaction with CO₂, Nd:YAG and HPDL effected very little change to the wettability characteristics of the PE. In contrast, interaction of the PE with excimer laser radiation resulted in a marked improvement in the wettability characteristics. After excimer laser treatment, the surface O₂ content was found to have increased and the material was seen to be more polar in nature, resulting in a significant increase in the wettability characteristics. The work has shown that the wettability characteristics of the PE could be controlled and/or modified with laser surface treatment. However, a wavelength dependence of the change in the wetting properties could not be deduced from the findings of this work.

Keywords: CO₂ laser, Nd:YAG laser, excimer laser, high-power diode laser (HPDL), polyethylene (PE), surface energy, wettability

1 INTRODUCTION

Much work has been carried out to study the effects of laser wavelength variation for medical and surgical applications, revealing clear differences in the performance and effectiveness of many different lasers for such applications. In contrast, comparisons of the differences in the beam interaction characteristics with various materials of the predominant materials processing lasers, the CO₂, the Nd:YAG and the excimer lasers, are limited. The main fundamental differences resulting from wavelength variations of CO, CO₂, Nd:YAG and excimer lasers for a number of materials processing applications have been detailed previously [1–4]. Likewise, such practical comparisons between these traditional materials processing lasers and the more contemporary high-power diode laser (HPDL) are even fewer in number [5, 6]. However, comprehensive investigations by Lawrence and co-workers compared

the effects of CO₂, Nd:YAG, excimer and HPDL radiation on the wettability characteristics of an Al₂O₃/SiO₂-based ceramic [7, 8] and a mild steel [9, 10], noting that changes in the wettability characteristics of the ceramic and the steel varied depending upon the laser type.

In general, polymer materials possess poor adhesion characteristics. Consequently it is very difficult to wet, and therefore bond, almost all polymer materials to adhesives without modifying their surface in order to improve their wettability characteristics. Traditionally a number of surface modification techniques have been employed to achieve such ends. Previously Fourche [11] investigated a number of mechanical and flame methods which essentially roughened the polymer surface thereby promoting improved mechanical bonding. A number of workers have developed chemical treatments primarily to increase the surface O₂ content of various polymer materials. These include oxidation in chromic acid [12] and sulphuration in chlorosulphonic acid [13]. However, these chemical treatments require prolonged immersion of the polymer materials in the acids in order to obtain any significant improvement in interfacial bond strength. What is more, these treatments are often accompanied by an undesirable loss in mechanical strength. Kaplan *et al.*

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[14] used the corona discharge treatment to modify the surface of ultra-high-strength polyethylene (UHSPE) fibres. Plasma treatments have also shown a good deal of promise for polymer material surface modification [15–19]. Nevertheless, despite the very beneficial improvements in interfacial shear strength that can be obtained from such plasma treatments, the actual process itself is extremely complex and consequently somewhat difficult to control.

Lasers, on the other hand, can offer the user not only an exceedingly high degree of process controllability, but also a great deal of process flexibility. Lawrence and Li have amply demonstrated the practicability of employing different types of lasers to effect changes in the wettability characteristics of ceramics [7, 8, 20] and metals [9, 10] for improved adhesion and bonding. In the case of polymer materials, excimer laser radiation has been shown to be a very effective means of enhancing their wettability characteristics. First demonstrated in 1982 by Srinivasan and Mayne-Banton [21], the excimer laser is typically used to remove thin surface layers of polymers. In recent years this technique has been applied to control precisely and alter the surface characteristics of a number of polymer materials such as polyethylene terephthalate (PET) in both film [22], fibre [23] and sheet [24, 25] form. Work on PET sheet [24] and poly-paraphenylene terephthalamide (PPTA) fibres [26] revealed that excimer laser treatment resulted in surface roughening. It was suggested that this was probably due to the differential etching of crystalline and amorphous regions in the material. A generally more undulating surface morphology, as opposed to a finely roughened surface, was observed by Heitz *et al.* [22] and Watanabe and Takata [26] after excimer laser treatment of PET films and fibres respectively. Both studies reported an increase in adhesion, citing the reason as being the occurrence of photochemical reactions which were accompanied by slight surface ablation. Similar improvements in adhesion strength of excimer laser treated polypropylene (PP) films were reported by Breuer *et al.* [27] when using certain optimum laser parameters. It was proposed that such improvements were the result of the laser generating a more polar surface. Laurens *et al.* [28, 29] also concluded that a more polar surface resulted from the excimer laser treatment of polyetheretherketone

(PEEK). Comprehensive and detailed investigations by Song and Netravali [30–32] into the effects of excimer laser radiation on the interfacial characteristics of UHSPE fibres and epoxy resin revealed a considerable increase in the interfacial shear strength after laser treatment. This was attributed to the increase in surface roughness, the increase in surface O₂ content and the increased polar nature of the fibres after excimer laser treatment. However, despite the large amount of work conducted with excimer lasers, no published literature exists to date pertaining to the use of other industrial lasers to modify the wettability characteristics of polymer materials.

This present work describes for the first time the beam interaction characteristics of a 1 kW CO₂ laser, a 400 W Nd:YAG laser, a 5 W KrF excimer laser and a 120 W HPDL with the biomaterial polyethylene (PE), focusing particularly on the differing effects of these lasers on the wettability characteristics. These chiefly incorporate contact angle variations, the differences in morphological and microstructural features, the chemical composition of the surface and the surface energy changes. Despite the fact that PE is widely used in surgery for total joint replacement, no published literature exists pertaining to wettability characteristics enhancement using lasers or other means.

2 EXPERIMENTAL PROCEDURES

2.1 Materials processing procedure

The solid materials used as substrates in the wetting experiments were cubes (25 × 25 mm² with a thickness of 5 mm) machined from a block of high-density PE. The contact surfaces of the materials were used as-received in the experiments. The general laser processing experimental arrangement comprised of the defocused laser beams being fired back and forth across the surfaces of the PE by traversing the samples beneath the laser beams of the four lasers using the *x* and *y* axis of the computer numerically controlled (CNC) gantry table. Impingement of the laser beams on the samples was perpendicular to their surface. The general operating characteristics of the lasers used in the study are detailed in Table 1. Both pulsed and continuous wave (CW) lasers

Table 1 Details of the selected industrial lasers used

Operating characteristic	CO ₂ laser	Nd:YAG laser	HPDL	Excimer laser
Active medium	CO ₂ gas	Nd:YAG crystal	GaAlAs	KrF gas
Wavelength	10.6 μm	1.06 μm	940 nm	248 nm
Maximum average output	1 kW	400 W	120 W	5 W
Maximum pulse energy	—	70 J	—	35 mJ
Pulse width	—	0.3–10 ms	—	20 ns
Repetition rate	—	1–1000 Hz	—	1–55 Hz
Fibre core diameter	—	600 μm	1 mm	—
Mode of operation	CW	Pulsed (rapid)	CW	Pulsed (multiple)
Beam diameter/size	6 mm	6 mm	6 mm	1.8 × 1.8 mm

were used in the study with the result that both the average power and the peak power of each laser will differ. Therefore, in order to achieve a reasonable comparison of the effects of each laser on the wettability characteristics of the PE, the laser energy density (fluence) of each laser beam incident on the PE surface was set by manipulating the laser power density and traverse speed in the case of the CO₂ laser and the HPDL, and the laser power density, pulse width and frequency in the case of the Nd:YAG and excimer lasers. The above properties were manipulated so that the energy density of each of the four lasers incident upon the PE surface was around 300 mJ/cm².

2.2 Contact angle and surface energy analysis procedures

To investigate the effects of laser radiation on the wetting and surface energy characteristics of the PE, wetting experiments were conducted. The experiments were comprised of control experiments carried out using the sessile drop technique with a variety of test liquids with known surface energy properties. Thus it was possible to quantify any surface energy changes in the PE resulting from laser interaction.

The sessile drop control experiments were carried out using glycerol, formamide, ethyleneglycol and dimethylsulphoxide; details of the test liquids can be found elsewhere [33]. The experiments were conducted in atmospheric conditions at a temperature of 20 ± 2 °C. The droplets were released in a controlled manner on to the surface of the test substrate materials (laser treated and untreated) from the tip of a micropipette, with the resultant volume of the drops being approximately 6 × 10⁻³ cm³. Each experiment lasted for 3 min with profile photographs of the sessile drops being obtained every minute. The contact angles were then measured with a mean value being subsequently determined. The standard deviation of the contact angles due to experimental error was calculated as being ±0.2°.

It was noted during the wetting experiments that, throughout the period of the experiments, no discernible change in the magnitude of the contact angle was observed, indicating that thermodynamic equilibrium was established at the solid–liquid interface at the

outset of the experiments. This is perhaps surprising considering the temperature effect on surface tension described by Mayers [34]. However, results similar to those observed in this study have been described by Agathopoulos and Nikolopoulos [35].

3 EFFECTS OF LASER RADIATION ON CONTACT ANGLE CHARACTERISTICS

As can be seen from Table 2, under the experimental laser parameters employed, laser irradiation of the surfaces of the PE samples resulted in changes in the contact angle. Table 2 shows clearly that such changes were dependent upon the laser used. It can be seen that in general, interaction of CO₂ radiation with the PE resulted in an increase in the contact angle between the PE and the control liquids, while interaction of the Nd:YAG laser and the HPDL with the PE radiation resulted in a slight reduction. In contrast, interaction of the excimer laser beam with the PE resulted in a considerable reduction in the contact angle between the PE and the control liquids.

3.1 Variations in surface roughness characteristics

According to Neumann and Good [36] and Neumann [37], a model similar to that for heterogeneous solid surfaces can be developed in order to account for surface irregularities, being given by a rearrangement of Wenzel's equation:

$$\gamma_{sl} = \gamma_{sv} - \left(\frac{\gamma_{lv} \cos \theta_w}{r} \right) \quad (1)$$

where γ_{sl} is the energy of the solid–liquid interface, γ_{sv} is the energy of the solid–vapour interface, γ_{lv} is the energy of the liquid–vapour interface, r is the roughness factor defined as the ratio of the real and apparent surface areas and θ_w is the contact angle for the wetting of a rough surface. It is clear from equation (1) that if the roughness factor, r , is large (around 1), i.e. the solid surface is smooth, then γ_{sl} will become small; hence, a reduction in the contact angle will be inherently realized by the liquid if $\theta < 90^\circ$. In contrast, if $\theta > 90^\circ$ then the opposite will be observed.

Table 2 Mean values of contact angles formed between the selected test liquids at 20 °C and the PE before and after laser treatment

Laser	Contact angle, θ (deg)			
	Glycerol	Formamide	Ethyleneglycol	Dimethylsulphoxide
Untreated	66.4	61.3	58.0	45.6
CO ₂	68.3	56.6	54.6	41.4
Nd:YAG	58.7	54.6	51.7	38.7
HPDL	67.0	55.2	52.4	40.5
Excimer	38.7	36.9	32.9	27.1

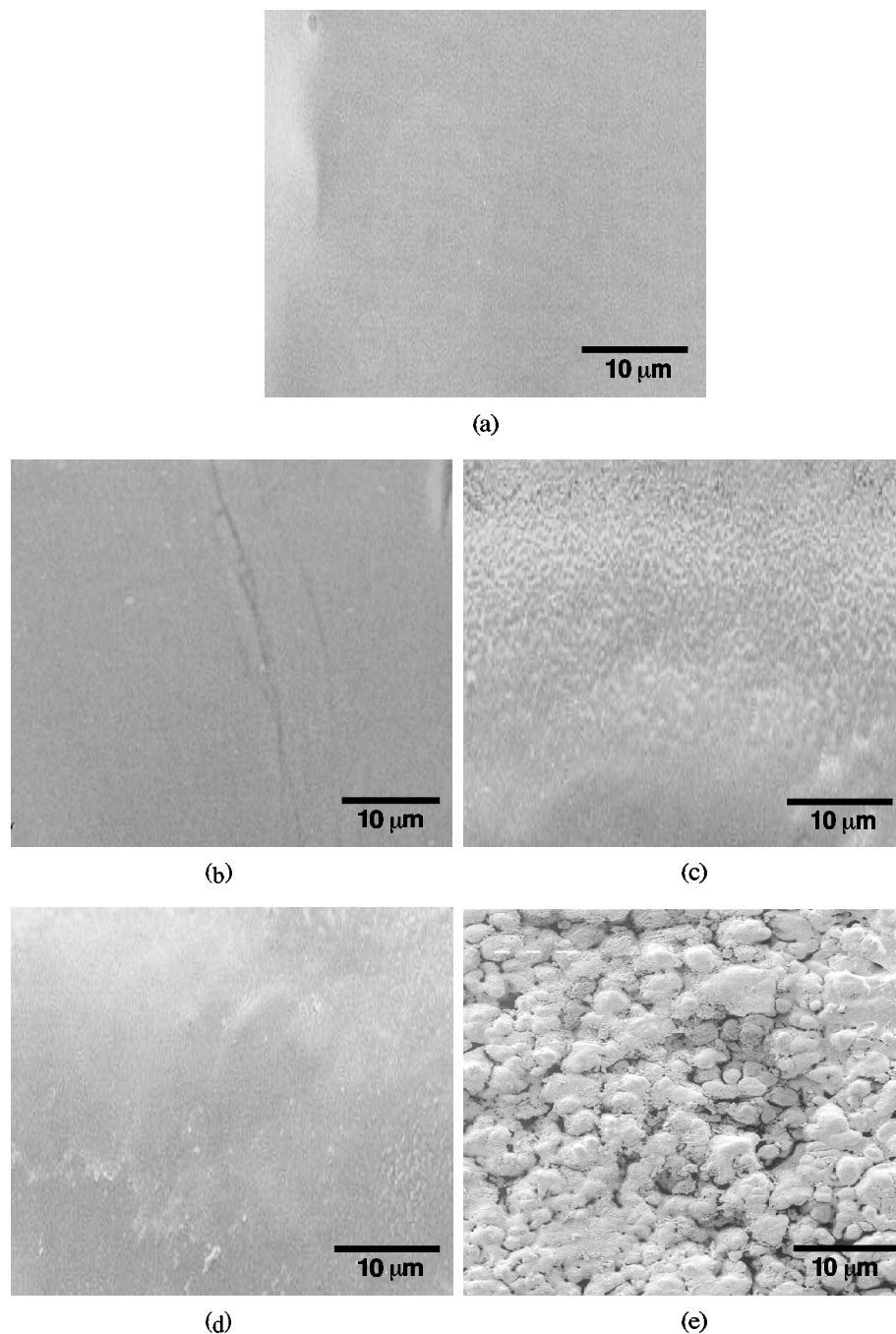


Fig. 1 Typical scanning electron micrograph surface images of the PE (a) before laser treatment and after interaction with (b) CO₂ laser, (c) Nd:YAG laser, (d) HPDL and (e) excimer laser radiation

The various surface effects of the respective lasers on the PE are clearly discernible from Fig. 1. From the micrographs shown in Fig. 1 it would appear that in the instances where CO₂, Nd:YAG and HPDL radiation was incident with the PE surface, surface melting and resolidification to varying degrees was induced. On the other hand, Fig. 1 shows that interaction of the PE with excimer laser radiation resulted in surface ablation. Analysis of the PE surface roughness (using a Taylor–Hobson Surtronic 3+ profilometer) after treatment

with these lasers revealed the surface roughness to have increased from an average roughness value R_a of 2.27 μm to a value of 2.46 μm (CO₂), 2.51 μm (Nd:YAG), 2.49 μm (HPDL) and 4.22 μm (excimer). Feng *et al.* [38] noted that under certain surface conditions, contact angle is inversely proportional to surface roughness. Clearly, this proposal is borne out somewhat by the CO₂, Nd:YAG and HPDLs, but does not hold in the case of the excimer laser. It is believed that the increase in surface roughness of the PE after excimer

laser treatment is counteracted by increases in the surface O_2 content and the surface energy changes (as discussed later in Sections 3.2 and 5).

3.2 Variations in surface oxygen content

The O_2 content of a material's surface is an influential factor governing the wetting performance of the material [39, 40]. Wetting is governed by the first atomic layers of the surface of a material. Thus, in order to determine element content of O_2 at the surface of the PE it was necessary to examine the surface using X-ray photo-emission spectroscopy (XPS).

Only very marginal differences in the surface O_2 content of the PE after interaction with the CO_2 , Nd:YAG and HPDL beams were observed. After treatment with these lasers the surface O_2 content of the PE altered slightly from an initial value of 12.8 at. % to 12.5 (CO_2), 12.4 (Nd:YAG) and 12.1 at. % (HPDL). Conversely, interaction of the PE with excimer laser radiation resulted in the surface O_2 content of the PE increasing markedly to 30.1 at. %.

4 SURFACE ENERGY AND THE DISPERSIVE/POLAR CHARACTERISTICS

The intermolecular attraction which is responsible for surface energy, γ , results from a variety of intermolecular forces whose contribution to the total surface energy is

additive [41]. The majority of these forces are functions of the particular chemical nature of a certain material, and as such the total surface energy comprises of γ^p (polar or non-dispersive interaction) and γ^d (dispersive component; since van der Waals forces are present in all systems regardless of their chemical nature). Therefore, the surface energy of any system can be described by equation (2) [41] (see the Appendix). Fowkes [41], and Agathopoulos and Nikolopoulos [35], have demonstrated that it is possible to estimate reasonably accurately the dispersive component of a material's surface energy, γ_{sv}^d , by plotting the graph of $\cos \theta$ against $(\gamma_{lv}^d)^{1/2}/\gamma_{lv}$ in accordance with equation (5) [41], with the value of γ_{sv}^d being estimated by the gradient, $2(\gamma_{sv}^d)^{1/2}$, of the line which connects the origin, $\cos \theta = -1$, with the intercept point of the straight line, $\cos \theta$ against $(\gamma_{lv}^d)^{1/2}/\gamma_{lv}$, correlating the data point with the abscissa at $\cos \theta = 1$. Figure 2 shows the best-fit plot of $\cos \theta$ against $(\gamma_{lv}^d)^{1/2}/\gamma_{lv}$ for the untreated and laser-treated PE–experimental control liquids system.

By comparing the ordinate intercept points of the untreated and laser-treated PE–liquid systems given in Fig. 2, it is evident that the best-fit straight lines for the PE–liquid systems of the CO_2 , Nd:YAG and HPDLs intercept the ordinate at similar points. Indeed, the intercept points of these PE–liquid systems for these lasers are close to the ordinate intercept point of the untreated PE. Conversely, the ordinate intercept point for the excimer laser PE–liquid system is considerably higher above the origin than those of the untreated, CO_2 , Nd:YAG and HPDL PE–liquid systems. This is of great importance

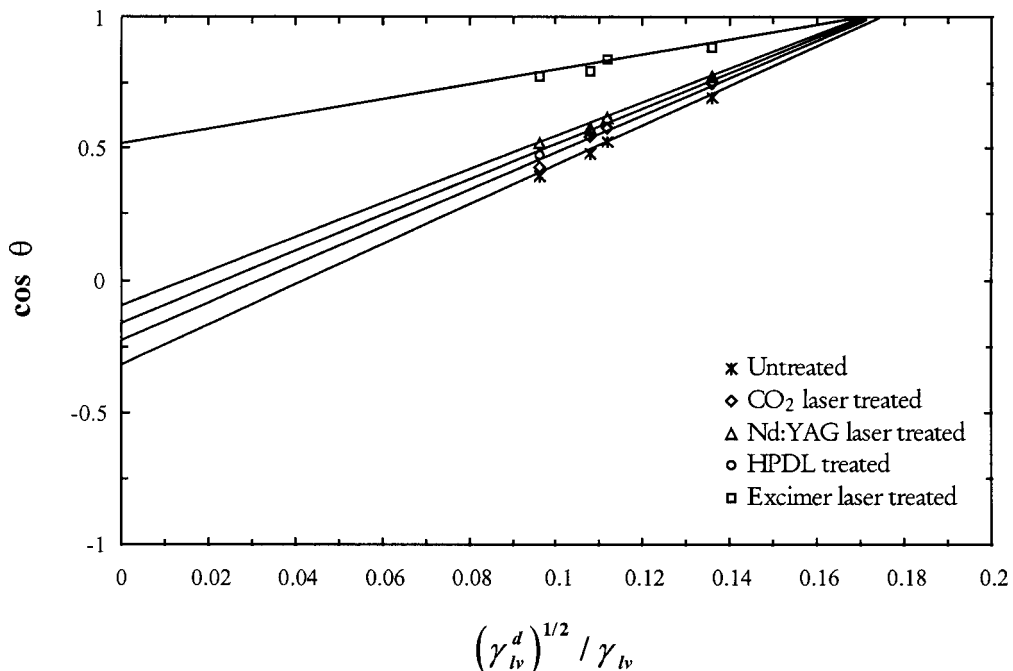


Fig. 2 Typical plot of $\cos \theta$ against $(\gamma_{lv}^d)^{1/2}/\gamma_{lv}$ for the untreated and laser-treated PE in contact with the test control liquids

Table 3 Values determined for the constants a and b from the plots of W_{ad} against W_{ad}^d for the PE before and after laser treatment

PE condition	a	b (10^{-3} J/m ²)
Untreated	1.14	-6.33
CO ₂ laser treated	1.16	-4.80
Nd:YAG laser treated	1.15	-13.69
HPDL treated	1.17	-1.69
Excimer laser treated	1.24	-19.69

since interception of the ordinate well above the origin is indicative of the action of polar forces across the interface, in addition to dispersion forces, hence improved wettability and adhesion is promoted. On the other hand, as the ordinate interception points approach the origin, the influence of polar forces diminishes and dispersion forces begin to dominate [41, 42]. Hence from Fig. 2 it can be asserted that polar forces are in attendance more in the excimer laser treated PE samples than those either untreated or treated with the other lasers. Furthermore, because none of the best-fit straight lines intercept below the origin, then it can be said that the development of an equilibrium film pressure of adsorbed vapour on the PE surface (untreated and laser treated) did not occur [41, 42].

Again, in accordance with studies conducted by Fowkes [41], and Agathopoulos and Nikolopoulos [35], it is not possible to determine the value of the polar component of the PE surface energy, γ_{sv}^p , directly from Fig. 2. This is because the intercept of the straight line [$\cos \theta$ against $(\gamma_{lv}^d)^{1/2}/\gamma_{lv}$] is at $2(\gamma_{sv}^p \gamma_{lv}^p)^{1/2}/\gamma_{lv}$, and thus only refers to individual control liquids and not the control liquid system as a whole, that is all four test liquids. However, it has been established that the entire amount of the surface energies due to dispersion forces either of the solids or the liquids are active in the wettability performance [41, 43]. As such, it is possible to calculate γ_{sv}^p using equations (6) to (10) (see the Appendix). Although equations (6) to (10) were originally introduced by Agathopoulos and Nikolopoulos [35] for use with ceramic/biological liquid systems, they have, nonetheless, been used previously by Lellig and Ondracek [33] and Chattoraj and Birdi [42] to study the wettability characteristics of a number of polymer materials, revealing that the use of these equations for such an analysis is valid. Thus, from the best-fit straight line plots of W_{ad} against W_{ad}^d for the PE when it is both

untreated and laser treated, it was possible to determine the constants a and b for each separate condition of the PE (see Table 3). Since γ_{sv}^d has already been determined for the untreated and laser-treated PE from Fig. 2, then it is possible to calculate γ_{sv}^p for untreated and laser-treated PE using equation (10).

As can be seen from Table 4, whereas CO₂, Nd:YAG and HPDL treatment of the surface of the PE effected only small increases in γ_{sv}^p , excimer laser treatment of the surface of the PE occasioned a marked increase in γ_{sv}^p . Such an increase in γ_{sv}^p of the PE is bound to have a positive effect upon the action of wetting and adhesion [41].

5 DISCUSSION OF LASER-AFFECTED WETTABILITY CHARACTERISTICS MODIFICATION

The results detailed previously show clearly that interaction of the selected industrial lasers with the PE has resulted in the contact angle formed between the control liquids altering to various degrees depending upon the laser type. Under the selected experimental laser operating parameters, interaction of the PE typically with the CO₂, Nd:YAG and HPDL beams effected very little change in the measured contact angles, while interaction of the PE with the excimer laser radiation occasioned considerable decreases in the measured contact angles. Such changes in the value of the contact angle are influenced, depending upon the laser used, primarily by: changes in the surface morphology; changes in the surface O₂ content and changes in the surface energy.

From Fig. 1 it can be seen that morphologies of the CO₂, Nd:YAG and HPDL-treated samples appear to be indicative of melting and resolidification. As is evident from the analysis of the surface roughness, the melting and subsequent resolidification after treatment with these lasers appears to have had very little effect on the surface roughness. In contrast, as shown in Fig. 1e, interaction of the PE with excimer laser radiation under the chosen operating parameters did not cause melting of the surface, but instead induced surface ablation which consequently resulted in a slightly rougher surface. Similar observations were made by Lawrence *et al.* [7] and Lawrence and Li [8–10] during surface treatment of ceramics and metals with excimer laser radiation. Additionally, Kokai *et al.* [44] have concluded that, with excimer laser parameters which are conducive to

Table 4 Determined surface energy values for the PE before and after laser irradiation

Surface energy component	Untreated	CO ₂ laser	Nd:YAG laser	HPDL	Excimer laser
Dispersive, γ_{sv}^d (mJ/m ²)	33.7	34.2	35.0	34.6	35.9
Polar, γ_{sv}^p (mJ/m ²)	3.26	4.32	3.88	4.47	10.21

the production of plumes, as was the case with the PE, then the surface roughness is increased as a result of plume-induced debris redepositing on the surface and excessive thermally induced surface fractures and porosities. Since plume generation was observed, then surface roughening after excimer laser irradiation was perhaps to be expected. However, Liu *et al.* [45], Nicolas *et al.* [46] and Henari and Blau [47], have reported that irradiating ZrO₂ with excimer laser radiation with energy densities in excess of 2.7 J/cm², resulted in a reduction in surface roughness. Such reductions were attributed to the fact that at these levels of energy density, melting of the ZrO₂ surface occurred.

According to equation (1) and the work of Feng *et al.* [38], an increase in the contact angle would be expected after interaction of the PE with the excimer laser. However, this is clearly not the case, as is apparent from Table 2 which shows that significant reductions in the contact angle were observed after excimer laser treatment. It is postulated that the increase in surface roughness of the PE after excimer laser treatment is counteracted to a large degree by the increases in the surface O₂ content and the surface energy changes. As discussed earlier, the surface O₂ content of the PE before and after treatment with the CO₂, the Nd:YAG and the HPDLs altered very little. However, after interaction with the excimer laser beam the surface O₂ content of the PE increased markedly. Such a finding is contrary to the findings of a number of workers [48, 49] who have noted that for ceramics, irradiation with an excimer laser beam creates defective energy levels, in particular the formation of O₂ vacancies. Nevertheless, the increase in surface O₂ content of polymer materials after excimer laser interaction is well documented [27–32]. Such an occurrence is due to the fact that polymers undergo main-chain scission when subjected to concentrated levels of ultraviolet radiation in air [50]. Thus, when exposed to the excimer laser radiation under the selected laser operating parameters, the PE can easily generate free radicals as transient species. The O₂ in the air can then react readily with the free radicals under the high temperatures generated on the surface of the PE. It is suggested that oxidation in this manner is the reason for the observed increase in the surface O₂ content of the PE after excimer laser treatment. Furthermore, the exhibited increase in the polar nature of the PE after excimer laser treatment can also be attributed to this photo-oxidation on the PE surface. As such, it is reasonable to assume that this surface oxidation will result in the generation of some surface O₂-containing polar functional groups [32].

By means of cross-sectional scanning electron microscopy (SEM) analysis it was possible to determine the laser melt/ablation depth in the PE samples for each laser. It was found that the depth of the laser melting, and in the case of the excimer laser, the ablation region, varied significantly according to laser type. For

the CO₂, Nd:YAG and HPDLs the melt depths were measured as 75, 31 and 67 μm respectively, while for the excimer laser the ablation depth was measured as 8 μm. As can be seen, the differences in laser melt/ablation depth obtained with the Nd:YAG laser and particularly the excimer laser, were smaller than those of the CO₂ laser or the HPDL. The main reason for these differences is thought to be due to the pulsed nature of the beams of the Nd:YAG and excimer lasers, as opposed to the CW nature of the CO₂ laser or HPDL beams. Since the interaction time of a pulsed beam with a material is much shorter than that of a CW beam, then consequently the depth of the laser melt/ablation region will be much smaller due to the reduced time afforded for heat transfer.

The excimer laser aside, the morphology of the PE generated after treatment with the CO₂ laser, the Nd:YAG laser and the HPDL was very similar. It is therefore possible to conclude that a wavelength dependence of the change in the wetting properties cannot be deduced from the findings of this work. This is apparent from the very similar properties of the surfaces irradiated with the CO₂, Nd:YAG and HPDLs, the wavelengths of which vary by more than an order of magnitude. Nonetheless, the work has shown that under the chosen experimental laser operating parameters, changes in the wettability characteristics of the PE were seen to alter to various degrees depending upon the laser type; in particular, whether the laser radiation had the propensity to cause melting or ablation of the surface. Consequently, it is therefore distinctly possible that pulse width may have played an important role.

6 CONCLUSIONS

Interaction of CO₂ laser, Nd:YAG laser, HPDL and excimer laser radiation with the surface of PE sheet was found to effect varying degrees of change to the wettability characteristics of the material. It was observed that interaction of the PE with CO₂, Nd:YAG and HPDL radiation resulted in very little change in the contact angle, and therefore the wettability characteristics, with the control liquids used. In contrast, interaction of the PE with excimer laser radiation occasioned a marked decrease in the contact angle, and therefore the wettability characteristics, with the control liquids used. Such changes after excimer laser treatment were identified as being primarily due to the increase in the surface O₂ content of the PE and the increase in the polar component of the surface energy. These occurrences are believed to be the result of photo-oxidation on the PE surface which, in turn, is assumed to have resulted in the generation of some surface O₂-containing polar functional groups, thus effecting the observed changes in the wettability characteristics of the PE after excimer laser treatment.

A wavelength dependence of the change in the wetting properties can not be deduced from the findings of this work. This is apparent from the very similar properties of the surfaces irradiated with the CO₂ laser, the Nd:YAG laser and the HPDL, the wavelengths of which vary by more than an order of magnitude. Nonetheless, the work has shown that under the chosen experimental laser operating parameters, changes in the wettability characteristics of the PE were seen to vary somewhat depending upon the laser type; in particular, whether the laser radiation had the propensity to cause surface melting or ablation. As such, the influence of pulse width cannot be discounted.

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APPENDIX

The surface energy of any system can be described by [41]

$$\gamma = \gamma^d + \gamma^p \quad (2)$$

Similarly, the work of adhesion, W_{ad} , can be expressed as the sum of the different intermolecular forces that act at the interface [41]:

$$W_{ad} = W_{ad}^d + W_{ad}^p = 2(\gamma_{sv}^d \gamma_{lv}^d)^{1/2} + 2(\gamma_{sv}^p \gamma_{lv}^p)^{1/2} \quad (3)$$

By equating equation (3) with the Young–Dupre equation then

$$W_{ad} = \gamma_{lv}(1 + \cos \theta) \quad (4)$$

and the contact angle for solid–liquid systems can be related to the surface energies of the respective liquid and solid by

$$\cos \theta = \frac{2(\gamma_{sv}^d \gamma_{lv}^d)^{1/2} + 2(\gamma_{sv}^p \gamma_{lv}^p)^{1/2}}{\gamma_{lv}} - 1 \quad (5)$$

The dispersive component of the work of adhesion, W_{ad}^d , can be expressed using only the relevant part of equation (3) thus

$$W_{ad}^d = 2(\gamma_{sv}^d \gamma_{lv}^d)^{1/2} \quad (6)$$

For each particular control liquid in contact with both the untreated and laser-treated PE surfaces, both W_{ad} and W_{ad}^d are related by

$$W_{ad} = aW_{ad}^d + b \quad (7)$$

where a and b are constants unique to each control liquid system. A linear relationship between the dispersive and polar components of the control test liquid's surface energies exists; thus

$$(\gamma_{lv}^p)^{1/2} = 0.45(\gamma_{lv}^d)^{1/2} + 1.85 \quad (8)$$

By introducing equation (7) into equation (3) and rearranging, then

$$W_{ad}^p = (a - 1)W_{ad}^d + b \quad (9)$$

or

$$(\gamma_{sv}^p)^{1/2}(\gamma_{lv}^p)^{1/2} = (a - 1)(\gamma_{sv}^d)^{1/2}(\gamma_{lv}^d)^{1/2} + \frac{b}{2} \quad (10)$$

Further, by introducing equation (8) into equation (10) and differentiating with respect to $(\gamma_{lv}^d)^{1/2}$, considering

that $(\gamma_{sv}^d)^{1/2}$ and $(\gamma_{sv}^p)^{1/2}$ are constant, then the following is valid:

$$(\gamma_{sv}^p)^{1/2} = \frac{(\gamma_{sv}^d)^{1/2}(a - 1)}{0.45} \quad (11)$$

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