Modification of the wettability characteristics of polymethyl methacrylate (PMMA) by means of CO_2, Nd:YAG, excimer and high power diode laser radiation

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Abstract

The surface of the bio-material polymethyl methacrylate (PMMA) was treated with CO_2, Nd:YAG, excimer and high power diode laser (HPDL) radiation. The laser radiation 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 CO_2, Nd:YAG and HPDL effected very little change to wettability characteristics of the PMMA. In contrast, interaction of the PMMA with excimer laser radiation resulted an increase in a marked improvement in the wettability characteristics. After excimer laser treatment the surface O_2 content was found to have increased and the material was seen to be more polar in nature. The work has shown that the wettability characteristics of the PMMA could be controlled and/or modified with laser surface treatment. However, a wavelength dependence of the change of the wetting properties could not be deduced from the findings of this work.

Keywords: CO_2 laser; Nd:YAG laser; Excimer laser; High power diode laser (HPDL); Polymethyl methacrylate (PMMA); Wettability

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1. Introduction

To date, 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 CO_2, the Nd:YAG and the excimer laser, are limited. Previously the main fundamental differences resulting from wavelength variations of CO, CO_2, Nd:YAG and excimer lasers for a number of materials processing applications have been detailed [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, in comprehensive investigations, Lawrence et al. compared the effects of CO_2, Nd:YAG, excimer and HPDL radiation on the wettability characteristics of an Al_2O_3/SiO_2 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 posses 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 thus promoting improved mechanical bonding. A number of workers have developed chemical treatments to primarily increase the surface O_2 content of various polymer materials [12, 13]. However, these chemical treatments are often accompanied by an undesirable loss in strength. Kaplan et al. [14] used the corona discharge treatment to modify the surface of ultra-high strength polythene (UHSPE) fibres. Plasma treatments have also shown a good deal of promise for polymer material surface modification. Holmes and Schwartz [15] studied the effect of ammonia plasma on UHSPE fibres and concluded that the adhesion of the fibres to epoxy resin was improved without the usual detrimental reduction in fibre strength. Li and Netravali [16-18] also investigated the effects of plasma (allylamine and ammonia) on UHSPE fibres and found that huge increases of over 300% in the interfacial shear strength were occasioned after some plasma treatments. Similar large increases in the interfacial shear strength of UHSPE fibres after plasma treatment were also observed by Nguyen et al. [19]. 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 and 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 precisely control and later the surface characteristics of a number of polymer materials. Much research has been carried out to study the effects of excimer laser radiation on the wettability characteristics of polyethylene terephthalate (PET) in both film [22], fibre [23] and sheet [24] form, as well as polyparaphenylene terephthalamide (PPTA) [25]. Improvements in the adhesion strength of excimer laser treated polypropylene (PP) films was reported by Breuer et al. [26] 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. [27, 28] also concluded that a more polar surface resulted from the excimer laser treatment of polyether-etherketon (PEEK). Furthermore, these workers found that the choice of laser wavelength has a crucial influence on the resultant wettability characteristics of the PEEK. Comprehensive and detailed investigations by Song and Netravali [29-31] 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 resulted after laser treatment. This enhancement in the interfacial shear strength was attributed to the increase in surface roughness, the increase in surface O_2 content and the increased polar nature of the fibres after excimer laser treatment. Yet, despite the large amount of work conducted with excimer lasers, no published literature to date exists pertaining to the use of other industrial lasers to modify the wettability characteristics of polymer materials.

This present work describes the beam interaction characteristics with the bio-material polymethyl methacrylate (PMMA) of a 1 kW CO_2 laser, a 400 W Nd:YAG laser, a 5 W KrF excimer laser and a 120 W HPDL, concentrating principally on the differing effects thereof 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 PMMA is used extensively in surgery as bone cement, no published literature exists regarding enhancement of the wettability characteristics using lasers or other means.

2. Experimental procedure

2.1. Materials processing procedures

The solid materials used as substrates in the wetting experiments were square blocks (50 mm x 50 mm with a thickness of 10 mm) of PMMA. 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 PMMA by traversing the samples beneath the laser beam using the x- and y-axis of the CNC gantry table. The general operating characteristics of the lasers used in the study are detailed in Table 1. Both pulsed and CW lasers were used in the study, therefore, both the average power and the peak power of each laser will differ. So, in order to reasonably compare the effects of each laser on the wettability characteristics of the PMMA, the laser energy density (fluence) of each laser beam incident on the PMMA surface was set by manipulating the laser power density and traverse speed in the case of the CO_2 laser and the HPDL, and the laser power density, pulse width and frequency in the case of the Nd:YAG and excimer lasers, such that the energy density of each of the four lasers incident upon the PMMA surface was around 300 mJ/cm^2.

2.2. Contact angle and surface energy analysis procedure

To investigate the effects of laser radiation on the wetting and surface energy characteristics of the PMMA 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 PMMA resulting from laser interaction. The sessile drop control experiments were carried out, using glycerol, formamide, ethyleneglycol and dimethylsulphoxide. Details of the test liquids are given elsewhere [32]. The experiments were conducted in atmospheric conditions at a temperature of 20^0C. The droplets were released in a controlled manner onto 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} cm^3. Each experiment lasted for three minutes 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 due to experimental error was calculated as being $\pm 0.2^0$.

It was observed 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 when one considers the temperature effect on surface tension as described by Mayers [33]. However, results similar to those observed in this study have been described by Agathopoulos et al. [34].

3. Theoretical background

3.1. Contact angle and wettability

When a drop of liquid is placed on a solid surface it may remain as a spherical drop, or spread to cover (wet) the solid surface [35]. The angle with which the liquid subtends the solid is known as the contact angle. In practice, for wetting to occur the contact angle is less than 90^0. If the contact angle is greater than 90^0 then the liquid does not wet the solid and no adhesion occurs [35]. When a drop of liquid is brought into contact with a flat solid surface, the final shape taken by the drop, and thus whether it will wet the surface or not, depends upon the relative magnitudes of the molecular forces that exist within the liquid (cohesive) and between the liquid and the solid (adhesive) [35]. The index of this effect is the contact angle θ, which the liquid subtends with the solid. θ is related to the solid and liquid surface energies, γ_{sv} and γ_{lv}, and the solid-liquid interfacial energy γ_{sl}, through the principle of virtual work expressed by the rearranged Young's equation:

$$\cos\theta = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}} \tag{1}$$

Clearly, to achieve wetting γ_{sv} should be large, while γ_{sl} and γ_{lv} should be small. Hence liquids of a lower surface tension will always spread over a solid surface of higher surface tension in order to reduce the total free-energy of the system [36]. This is due to fact that the molecular adhesion between solid and liquid is greater than the cohesion between the molecules of the liquid [35].

The adhesion energy of a liquid to a solid surface (the work of adhesion) W_{ad}, is given by the Young-Dupre equation:

$$W_{ad} = \gamma_{lv}(1 + \cos\theta) \tag{2}$$

It is also important to consider the influence of the substrate surface roughness on the wetting contact angle. Rough grooves on a surface, which may contribute to the influence of contact angles, can be categorised as either radial or circular grooves. Any practical rough surface can be represented by a combination of these two cases [37]. In fact two roughness parameters can be defined: the Wenzel type, D_R [38] and the Cassie/Baxter type, F_R [39] In the case that wetting spreads radially, as is the likely case with the laser treated PMMA, then the resulting radial contact angle, θ_{rad}, is related to the theoretical contact angle, θ_{th}, by

$$\cos\theta_{rad} = D_R(1 - F_R)\cos\theta_{th} - F_R \tag{3}$$

According to Neumann [40], only if F_R is equal to zero, then a model similar to that for heterogeneous solid surfaces can be developed in order to account for surface irregularities, being given by Wenzel's equation:

$$r(\gamma_{sv} - \gamma_{sl}) = \gamma_{lv}\cos\theta_w \tag{4}$$

where 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 important to note that Wenzel's treatment is only effective at the position of wetting triple line [37]. Nevertheless, it is evident from Eq. (4) that if the roughness factor, *r*, is large, that is the solid surface is smooth, then γ_{sl} will become small, thus, a reduction in the contact angle will be inherently realised by the liquid if $\theta_w<90^0$. Conversely, if $\theta_w>90^0$ then the opposite will be observed.

3.2. Surface energy and the polar/dispersive 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 [35]. 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 [35]

$$\gamma = \gamma^d + \gamma^p \tag{5}$$

Similarly, W_{ad} can be expressed as the sum of the different intermolecular forces that act at the interface [35]:

$$W_{ad} = W_{ad}^d + W_{ad}^p = 2\left(\gamma_{sv}^d \gamma_{lv}^d\right)^{1/2} + 2\left(\gamma_{sv}^p \gamma_{lv}^p\right)^{1/2} \tag{6}$$

By equating Eq. (6) with Eq. (2), the contact angle for solid-liquid systems can be related to the surface energies of the respective liquid and solid by

$$\cos\theta = \frac{2\left(\gamma_{sv}^d \gamma_{lv}^d\right)^{1/2} + 2\left(\gamma_{sv}^p \gamma_{lv}^p\right)^{1/2}}{\gamma_{lv}} - 1 \tag{7}$$

4. Effects of laser radiation on contact angle characteristics

As one can see from Table 2, under the experimental laser parameters employed, laser irradiation of the surfaces of the PMMA 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 the PMMA with CO_2, Nd:YAG and HPDL radiation resulted in decreases in the contact angle between the PMMA and the control liquids. In contrast, interaction of the PMMA with the excimer laser beam resulted in the contact angle between the PMMA and the control liquids reducing.

4.1. Variations in surface roughness characteristics

The various surface effects of the respective lasers on the PMMA are clearly discernible from Fig. 1. From the micrographs shown in Fig. 1 it would appear that in the instances where CO_2, Nd:YAG and HPDL radiation was incident with the PMMA surface, surface melting and resolidification to varying degrees was induced. On the hand, Fig. 1 shows that interaction of the PMMA with excimer laser radiation resulted in surface ablation. Analysis of the PMMA surface roughness (using a Taylor-Hobson Surtronic 3+ profileometer) after treatment with these lasers revealed the surface roughness to have increased from 1.95 μm to 2.18 μm (CO_2), 2.22 μm (Nd:YAG), 2.24 μm (HPDL) and 3.85 μm (excimer). Feng et al. [41] noted that under certain surface conditions, contact angle is inversely proportional the surface roughness. Clearly this proposal is borne out somewhat by the CO_2, Nd:YAG and HPDL's, but does not hold in the case of the excimer laser. It is believed that the increase in surface roughness of the PMMA after excimer laser treatment is counteracted by increases in the surface O_2 content and the surface energy changes (as discussed later).

4.2. 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 [42, 43]. 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 PMMA it was necessary to examine the surface using x-ray photoemission spectroscopy (XPS). Only very marginal differences in the surface O_2 content of the PMMA 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 PMMA altered slightly from an initial value of 14.7at.% to 14.5at.% (CO_2), 14.9at.% (Nd:YAG) and 14.7at.% (HPDL). Conversely, interaction of the PMMA with excimer laser radiation resulted in the surface O_2 content of the PMMA increasing markedly to 37.7at.%.

5. Surface energy and the dispersive/polar characteristics

In accordance with studies conducted by Fowkes [35] and Agathopoulos et al. [34], it is possible to estimate reasonably accurately the dispersive component of the PMMA surface energy, γ_{sv}^{d}, by plotting the graph of cos θ against $(\gamma_{lv}^{d})^{1/2}/\gamma_{lv}$ in accordance with Eq. (7) [35], 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 θ against $(\gamma_{lv}^{d})^{1/2}/\gamma_{lv}$) correlating the data point with the abscissa at cos $\theta = 1$. Fig. 2 shows the best-fit plot of cos θ against $(\gamma_{lv}^{d})^{1/2}/\gamma_{lv}$ for the untreated and laser treated PMMA-experimental control liquids system.

By comparing the ordinate intercept points of the untreated and laser treated PMMA-liquid systems given in Fig. 2, it is evident that the best-fit straight lines for the PMMA-liquid systems of the CO_2, Nd:YAG and HPDL intercept the ordinate at similar points. Indeed, the intercept points of these PMMA-liquid systems for these lasers are close the ordinate intercept point of the untreated PMMA. Conversely, the ordinate intercept point for the excimer laser PMMA-liquid system is considerably higher above the origin than those of the untreated, CO_2, Nd:YAG and HPDL PMMA-liquid systems. This is of great importance 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 approaches the origin, the influence of polar forces diminishes and dispersion forces begin to dominate [35, 44]. Thus, from Fig. 2 it can be asserted that polar forces are in attendance more in the excimer laser treated PMMA 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 PMMA surface (untreated and laser treated) did not occur [35, 44].

Again, in accordance with studies conducted by Fowkes [35] and Agathopoulos et al. [34], it is not possible to determine the value of the polar component of the PMMA surface energy, γ_{sv}^{p}, directly from Fig. 2. This is because the intercept of the straight line (cos θ against $(\gamma_{lv}^{d})^{1/2}/\gamma_{lv}$) is at $2\left(\gamma_{sv}^{p}\gamma_{lv}^{p}\right)^{1/2}/\gamma_{lv}$, and thus only refers to individual control liquids and not the control liquid system as a whole. 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 [35, 45]. As such, it is possible to calculate the dispersive component of the work of adhesion, W_{ad}^{d}, using only the relevant part of Eq. (6) thus

$$W_{ad}^{d} = 2\left(\gamma_{sv}^{d}\gamma_{lv}^{d}\right)^{1/2} \tag{8}$$

The results reveal that for each particular control liquid in contact with both the untreated and laser treated PMMA surfaces, both W_{ad} and W_{ad}^{d} are related by the straight line relationship

$$W_{ad} = aW_{ad}^{d} + b \tag{9}$$

where a and b are constants unique to each control liquid system. Also, for the control test liquids used, a linear relationship between the dispersive and polar components of the control test liquids surface energies has been deduced which satisfies the equation

$$\left(\gamma_{lv}^{p}\right)^{1/2} = 0.45\left(\gamma_{lv}^{d}\right)^{1/2} + 1.85 \tag{10}$$

By introducing Eq. (9) into Eq. (6) and rearranging, then

$$W_{ad}^{p} = (a-1)W_{ad}^{d} + b \tag{11}$$

By introducing Eq. (10) into Eq. (11) and differentiating with respect to $\left(\gamma_{lv}^{d}\right)^{1/2}$, then the following can be derived:

$$\left(\gamma_{sv}^{p}\right)^{1/2}=\frac{\left(\gamma_{sv}^{d}\right)^{1/2}(a-1)}{0.45} \tag{12}$$

Although Eqs. (9) -(12) were originally introduced by Agathopoulos et al. [34] for use with ceramic/biological liquid systems, they have, nonetheless, been used previously by Lellig and Ondracek [32] 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 PMMA when it is both untreated and laser treated, it was possible to determine the constants *a* and *b* for each separate condition of the PMMA (see Table 3). Since γ_{sv}^{d} has already been determined for the untreated and laser treated PMMA from Fig. 2, then it is possible to calculate γ_{sv}^{p} for untreated and laser treated PMMA using Eq. (12). The values for both γ_{sv}^{d} and γ_{sv}^{p} for untreated and laser treated PMMA are given in Table 4. For the untreated PMMA the values of γ_{sv}^{d} and γ_{sv}^{p} are in close agreement with those found by Lellig and Ondracek [32]. As one can see from Table 4, whereas CO_2, Nd:YAG and HPDL treatment of the surface of the PMMA effected only a small increases in γ_{sv}^{p}, excimer laser treatment of the surface of the PMMA occasioned a marked increase in γ_{sv}^{p}. Such an increases in γ_{sv}^{p} of the PMMA is bound to have a positive effect upon the action of wetting and adhesion [35].

6. Discussion of laser effected wettability characteristics modification

The results detailed previously show clearly that interaction of the PMMA with the selected industrial lasers 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 PMMA typically with the CO_2, Nd:YAG and HPDL beams effected very little change in the measured contact angles, whilst interaction of the PMMA 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 O_2 content and changes is the surface energy.

From Fig. 1 it can be seen that the morphologies of the CO_2, 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 one can see from Fig. 1(e), interaction of the PMMA 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. [7-9] during surface treatment of ceramics and metals with excimer laser radiation. Additionally, Kokai et al. [46] have concluded that, with excimer laser parameters which are conducive to the production of a plume, as was the case with the PMMA, 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. [47], Nicolas et al. [48] and Henari et al. [49], have reported that irradiating ZrO_2 with excimer laser radiation with energy densities in excess of 2.7 J/cm^2, resulted in a reduction in surface roughness. Such reductions were attributed to the fact that at these levels of energy density, melting of the ZrO_2 surface occurred.

According to Eq. (1) and the work of Feng et al. [41], an increase in the contact angle would be expected after interaction of the PMMA 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 PMMA after excimer laser treatment is counteracted to a large degree by the increases in the surface O_2 content and the surface energy changes. As was discussed earlier, the surface O_2 content of the PMMA before and after treatment with the CO_2, the Nd:YAG and the HPDL's altered very little. But, after interaction with the excimer laser beam the surface O_2 content of the PMMA increased markedly. Such a finding is contrary to those of a number of workers [50, 51] who have noted that for ceramics, irradiation with an excimer laser beam creates defective energy levels, in particular the formation of O_2 vacancies. Nevertheless, the increase in surface O_2 content of polymer materials after excimer laser interaction is well documented [26-31]. Such an occurrence is due to the fact that polymers undergo main-chain scission when subjected to concentrated levels of UV radiation in air [52]. Thus, when exposed to the excimer laser radiation under the selected laser operating parameters, the PMMA can easily generate free radicals as transient species. The O_2 in the air can then react readily with the free radicals under the high temperatures generated on the surface of the PMMA. It is suggested that oxidation in this manner is the reason for the observed increase in the surface O_2 content of the PMMA after excimer laser treatment. Furthermore, the exhibited increase in the surface energy, in particular the increased polar nature of the PMMA after excimer laser treatment, can also be attributed to this photo-oxidation on the PMMA surface. As such, it is reasonable to assume that this surface oxidation will result in the generation of some surface O_2-containing polar functional groups [31]. On the other hand, it is asserted that the decreases in contact angle experienced by the PMMA after treatment with the CO_2, the Nd:YAG and the HPDL are due in no small measure to the decreases in the surface roughness after treatment with these lasers.

By means of cross-sectional SEM analysis it was possible to determine the laser melt/ablation depth in the PMMA 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 CO_2, Nd:YAG and HPDL the melt depths were measured as 56 μm, 24 μm and 53 μm respectively, whilst for the excimer laser the ablation depth was measured as 12 μm. As one can see, the differences in laser melt/ablation depth obtained with the Nd:YAG and particularly the excimer laser, were smaller than those of the CO_2 or 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 CO_2 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 owing to the reduced time afforded for heat transfer.

The excimer laser aside, the morphology of the PMMA generated after treatment with the CO_2, the Nd:YAG and the HPDL was very similar. It is therefore possible to conclude that a wavelength dependence of the change of 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 CO_2, the Nd:YAG 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 PMMA 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.

7. Conclusions

Interaction of CO_2 laser Nd:YAG laser, high power diode laser (HPDL) and excimer laser radiation with the surface of polymethyl methacrylate (PMMA) sheet was found to effect varying degrees of change to the wettability characteristics of the material. It was observed that interaction of the PMMA with CO_2, 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 PMMA 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 O_2 content of the PMMA and the increase in the polar component of the surface energy. These occurrences are believed to be the result of photo-oxidation on the PMMA surface which, in turn, is assumed resulted in the generation of some surface O_2-containing polar functional groups, thus effecting the observed changes in the wettability characteristics of the PMMA after excimer laser treatment.

A wavelength dependence of the change of 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 CO_2 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 PMMA 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.

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Table 1. Details of the selected industrial lasers used.

Operating Characteristic	Laser			
	CO_2	**Nd:YAG**	**HPDL**	**Excimer**
Active Medium	CO_2 gas	Nd:YAG crystal	GaAlAs	KrF gas
Wavelength	10.6 μm	1.06 μm	810 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	~	600μm	~	~
Mode of Operation	CW	Pulsed (rapid)	CW	Pulsed (multiple)
Beam Diameter/Size	6 mm	6 mm	6 mm	1.8 x 1.8 mm

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

Laser	Contact Angle, θ (degrees)			
	Glycerol	**Formamide**	**Ethylenglycol**	**Dimethylsulphoxide**
Untreated	69.5	62.2	58.6	41.4
CO_2	65.4	58.6	54.9	38.4
Nd:YAG	66.9	60.2	56.1	39.6
HPDL	63.5	56.8	53.1	36.9
Excimer	42.1	38.0	35.3	23.6

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

PMMA condition	**a**	**b (mJ/m^2)**
Untreated	1.12	-2.88
CO_2 laser treated	1.15	-4.47
Nd:YAG laser treated	1.16	-2.07
HPDL treated	1.18	-6.08
Excimer laser treated	1.30	-20.86

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

		Laser			
Surface Energy Component	**Untreated**	**CO_2**	**Nd:YAG**	**HPDL**	**Excimer**
Dispersive, (γ_{sv}^{d}) (mJ/m^2)	37.2	38.6	38.1	39.1	40.1
Polar, (γ_{sv}^{p}) (mJ/m^2)	2.65	4.28	4.81	6.26	17.82

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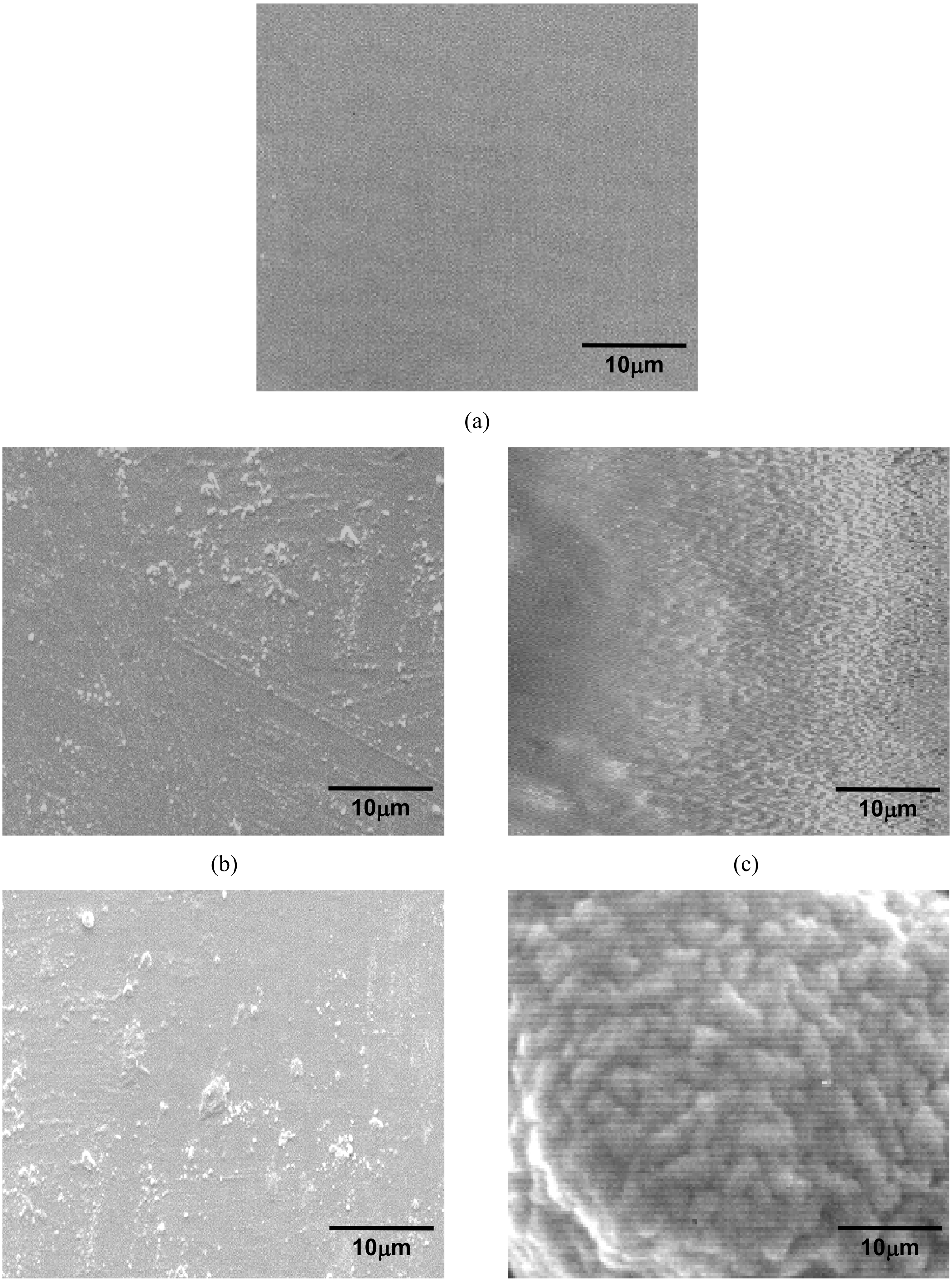
Fig. 1. Typical SEM surface images of the PMMA (a) before laser treatment and after interaction with (b) CO_2 laser, (c) Nd:YAG laser, (d) HPDL and (e) excimer laser radiation.



(a)

(b) (c)

(d) (e)

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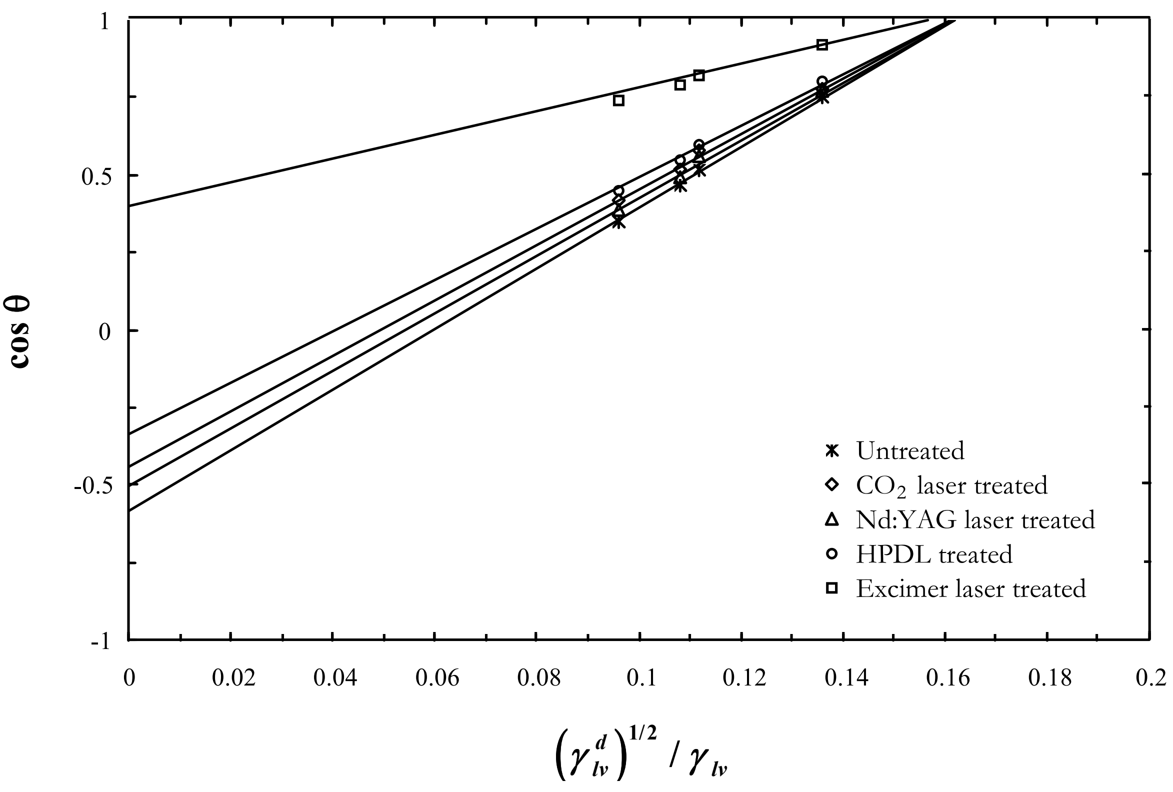
Fig. 2. Typical plot of cos θ against $\left(\gamma_{lv}^{d}\right)^{1/2}/\gamma_{lv}$ for the untreated and laser treated PMMA in contact with the test control liquids.



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