A characteristic modification of the surface topography of highly absorbing and oriented synthetic fibers such as PET, PA, or aromatic polyamides was found after irradiation with pulsed UV excimer lasers. In a range of moderate fluences from below the ablation threshold (about 30 mJ/cm² for PET) up to more than 150 mJ/cm² the originally smooth surface of these fibers changes to a rather regular roll-like structure on the micrometer scale, perpendicular to the fiber axis, after irradiation. This basic effect has a marked potential to modify various surface properties of fibers, which affect, e.g., their optical properties and coating or particle adhesion.

The effect of laser-induced micro-roughness of textile fibers on adhesion and capture of micrometer-sized particles

Thomas Bahners, Klaus Opwis, Torsten Textor, Win Labuda and Eckhard Schollmeyer

Studies of wet-filtration efficiency as well as dust separation in industrial filter facilities revealed that particle capture, especially in the micrometer range, was enhanced by the characteristic surface topography of the laser treated fibers. In the SEM analyses of the filters, it was observed that a large amount of very fine grain, i.e. submicrometer dust particles, was captured, which normally would not be captured on the smooth fiber surfaces of commercial filters. Based on this same effect on particle adhesion, laser-treated wiping cloth showed a markedly increased wiping efficiency. Thus it may be concluded that small particles captured in the grooves of the roll-like surface structure experience higher adhesion forces than on a smooth fiber surface.

Keywords: Surface modification, textile fibers, UV-light, excimer laser, particle adhesion, wiping

Introduction

The chemical and physical surface properties of textile fibers govern the friction, wetting behavior, adsorption ability, and adhesion characteristics not only of the fiber itself, but of the whole woven or non-woven textile structure. Thus, appropriate techniques to secure a certain macroscopic behavior of textiles in further processing as well as in use form an important part of textile finishing.

Because of aspects such as versatility, no environmental impact, and reduced use of chemical agents, physical processes for surface modification are of increasing interest. Besides gas discharge (plasma), photon-based processes form a promising alternative to conventional finishing. The present paper concentrates on the potential of pulsed UV excimer lasers for topographic surface modification.

A characteristic modification of surface topography of highly absorbing and oriented synthetic fibers such as poly(ethylene terephthalate) (PET), polyamide (PA), or aromatic polyamides was found after irradiation with pulsed UV excimer lasers [1-4]. Following irradiation, the originally smooth surface of these fibers changes to a rather regular roll-like structure on the micrometer scale, perpendicular to the fiber axis (Figure 1). This basic effect has a marked potential to modify various surface properties of the fiber, which affect, e.g., optical properties and coating or particle adhesion, the latter being the topic of this work.

Particle adhesion, in general, is governed by van der Waals, electrostatic and hydrogen bonding interactions. Considering a simple geometry one may conclude that the following holds for particles impacted on a fiber surface:

- Large particles adhere strongly to smooth surfaces, whereas the contact area and, accordingly, the adhesion force will be decreased in the case of micro-rough surfaces.

- Small particles experience higher contact area following roughening of the surface and accordingly an increase of the adhesion force.

With this background, the experimental studies reported here had the objective to evaluate the effect of the laser modified fiber surfaces on particle adhesion with regard to wet-filtration, dust filtration and wiping efficiency of textiles.

Surface Modification of synthetic fibers by eximer laser irradiation

The excimer laser irradiation of synthetic fibers made of highly absorbing polymers, e.g. aromatic polymers such as poly(ethylene terephthalate) (PET) and aromatic polyamides as well as aliphatic polymers such as polyamide-6 and -6.6 (PA), can generate a characteristic modification of the fiber surface. At moderate fluences ranging from below the ablation threshold (about 30mJ/cm² for PET) up to more than 150mJ/cm² the originally smooth surface of these fibers changes to a rather regular roll-like structure, perpendicular to the fiber axis, after irradiation with several excimer laser pulses. Typical absorption coefficients of these polymers at the wavelengths of commercial ArF and KrF excimer lasers (193 and 248 nm, respectively) are on the order of 10^5 cm^{-1}.

According to present understanding, this surface modification is caused by thermomechanical effects due to the extremely high energy deposition by the laser pulses [3,4]. A distinctive temperature profile is generated at the fiber surface. In the time scale involved, heat dissipation can be neglected and the temperature profile regarded as constant. For PET the temperature at the surface was estimated to be in excess of 2000 K (cf. also [5]). Ablation occurs where the temperature is in excess of the degradation temperature T_d of the polymer. Where the temperature is lower than T_d but higher than the melting point T_m, a layer of molten material would form allowing relaxation of the very high internal stress fields

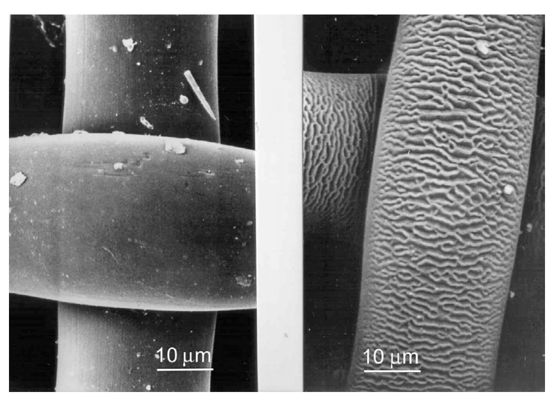

Figure 1 Scanning electron micrographs of PET fibers before (left) and after (right) UV-laser irradiation (248 nm, 10 pulses).

present in commercial fibers. A rough calculation gives a thickness of this layer of molten material of about 0.1 µm. It is assumed that in these far-from-equilibrium conditions the coupling of thermal and elastic shear fields creates co-operative transport phenomena resulting in the characteristic surface structure (Figure 2). Estimated values of important physical parameters for irradiation of PET at 193 nm are given in Table 1.

The resulting surface morphology can be described as a characteristic arrangement of 'rolls' (cf. Figure 1), separated by a mean distance <D>. Their overall orientation is strictly perpendicular to the orientation of the fiber fibrils – 'stress axis' - which is due to mechanical stress during the spinning process. The mean roll distance <D> is governed by the material as well as process parameters: The material defines the absorption at the given laser wavelength as well as the orientation of the macromolecules. For a certain wavelength, the number of laser pulses applied is the main process parameter. As a matter of fact, the laser fluence, i.e. pulse energy per unit area, is of little influence.

As exemplified in Figure 3 the absorption of radiation as a function of the wavelength is a prime parameter of the process. While the described micro-structures are generated at the stated wavelengths as well as in the VUV region, i.e. at 157 nm, a coarse structure is obtained at 308 nm using a XeCl excimer laser, which may be caused by the thermal damage due to the low absorption of PET at longer UV wavelengths.

The second influential parameter is the orientation of the polymer chains, i.e. the existence of - internal or externally applied - stress fields in the polymeric material. These was shown by experiments using partially oriented PET fibers and films [6] as well as fibers made of a polyurethane elastomer [7] (Figures 4 and 5). While a threshold fluence is a well-known characteristic of UV excimer laser induced ablation of polymers (cf. e.g. [8]), the stated studies showed that the formation of the surface structure not only has a threshold with regard to laser fluence, but also with regard to draw ratio. Only above a certain draw ratio, the UV-laser irradiation effects a morphological modification. The minimum draw ratio varies with the fluence and vice versa (Figure 5).

- absorption on the order of 105 cm-1
- energy deposition 10 to 20 kJ/cm³
- penetration depth approx. 0.1 µm
- time scale of energy deposition 10 to 30 ns
- time of thermo-physical processes approx. 100 ms
- resulting surface temperature ≈ 2000 K

Table 1

The third, purely experimental, parameter is the number of laser pulses applied. Characteristically <D> exhibits a strong dependence up to ten pulses applied with a saturation above about 20 pulses (Figure 6). At a given wavelength, the dependence of the mean roll distance <D> on the number of pulses, NP, could be described by the logarithmic expression

$$\{D\} = K1 \bullet \log NP + K2 \qquad (1)$$

in all investigated cases, where <D> was taken as the mean value over 10 to 20 rolls. For given conditions K1 and K2 are constant. K1 is weakly dependent on laser fluence, but is sen-

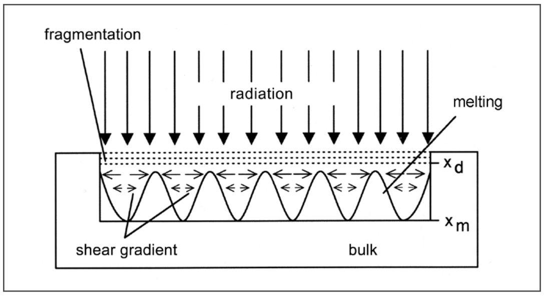

Figure 2 Schematic presentation of the various states of an irradiated polymer as a function of penetration depth. The parameters xd and xm denote the penetration depths, where the polymer is heated to the degradation td and the melting temperature tm, respectively.

sitive to the given penetration depth, i.e. to absorption coefficient and wavelength of the laser and specific fiber properties (e.g. draw ratio, see below). In this numerical expression, K2 is equivalent to the roll distance <D> after the first laser shot .

Experimental

The samples used in this work were fabrics made of poly(ethylene terephthalate) (PET) of various constructions. Depending on the actual application, these were non-wovens, woven or knitted fabrics. The samples were irradiated using a pulsed UV laser (Lambda-Physik 325 iCC) which was operated with KrF laser gas. The emitted wavelength using this gas is 248 nm. Depending on the application, the fabrics were irradiated either on a laboratory stage or for large sizes on a pilot setup described elsewhere [3].

Determination of wet-filtration properties

The wet-filtration properties were determined by measuring the separation of monodisperse suspensions of polystyrene latex particles. For the experiments, the fabric samples were installed in filter housings, through which the suspensions flowed. The flow was driven only by gravity.

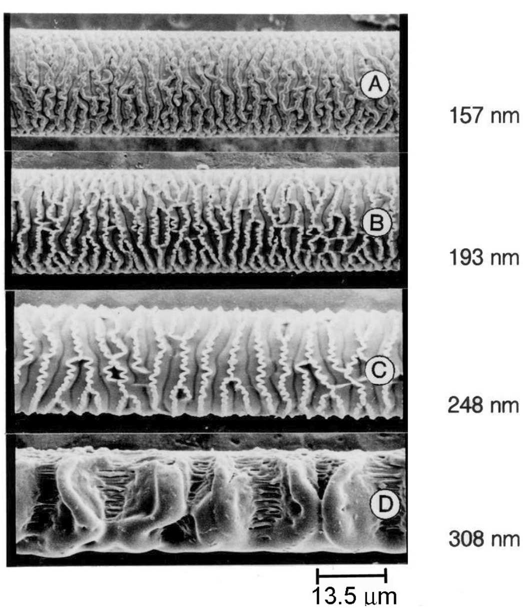

Figure 3 SEM micrographs of PET fibers, which were irradiated at various wavelengths. In each case 20 pulses at a fluence of 150 mJ/cm² were applied.

The fabric sample size – i.e. filter diameter - was 44 mm. The measurement was made individually for particles of 2, 5, 10 and 16 µm diameter. The particle concentrations before and after filtration were determined using a Coulter Counter®. The separation efficiency for each particle size T(d) [%] was calculated by

$$T(d) = 100 \bullet \{ 1- c_f(d) / c_0(d)\}$$

where $c_0(d)$ and $c_f(d)$ give the particle concentrations before and after filtration for the different particle sizes, respectively.

Determination of dust filtration efficiency

The dust filtration efficiency of modified filter materials was determined in industrial tests in a cotton mill, where the fabrics were used in a life-size filter. Again, the separation efficiency T(d) was calculated by eq.(2). The size-dependent particle concentrations were measured by optical particle analyzers based on Mie-scattering.

Determination of wiping efficiency

In order to determine the wiping efficiency of laser modified cloth, a special wiping test was devised. Fluorescent particles of defined sizes were applied to a silicon wafer and counted in an optical microscope. The wafer was then cleaned in a defined procedure which is sketched in Figure 7. The wiping was effected by towing a sled of defined weight, to which the sample cloth was fitted, along the surface. In order to simulate the conditions of manual wiping, a foam absorber was placed between the sled and the sample cloth. This way, 'soft' pressure similar to the human finger was executed over the whole area of the sample. The number of remaining particles was again determined by counting.

Results

Wet-filtraion

In order to investigate the effect of laser modification on the adhesion of particles to textile fibers in wet-filtration, textile samples were irradiated and exposed to latex suspension. In all stated cases, the irradiation produced structures with a mean roll distance <D> of 2.5 µm.

The experimentally determined filtration ef-

ficiency of a sieving fabric (plain weave, single layer) in original and laser treated forms is given in Figure 8. The data exemplify the effect of the laser treatment on the separation of suspended latex particles. Considering the statistical error in the data, a significant modification of the separation efficiency is observed, with an increase of T(d) for particles with a diameter of 5 µm and a decrease for larger particles (d ≈10 µm). The cut-size of the sample – i.e. the particle size for which T(d) = 50 % - is shifted to larger particle sizes by the laser treatment. As is the case for the original, 'as-received' sample, the particles larger than the mesh opening of the fabric are separated by the laser treated fabric to 100 %. In addition, SEM analysis of another sample – PET sieving fabric with a mean mesh opening of 10 µm - reveals that while bigger particles are captured by blocking, i.e. one or more particles effectively closing a mesh opening, particles much smaller than the mesh opening of the fabric impact on the fiber surface and are captured in the grooves of laser-induced roll structure (Figure 9).
In order to explain this experimental result,

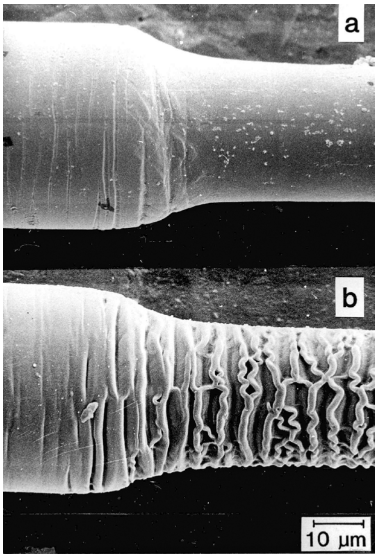

Figure 4 Development of laser-induced surface modification on a partially oriented PET yarn (POY) [8]: (a) SEM micrograph of an oriented zone of fiber, which has been generated through cold drawing ('neck-effect'). The polymer chains in the neck have higher orientation than outside. (b) SEM micrograph of the neck after laser treatment. The laser induced surface modification occurs only where the polymer chains are highly oriented, i.e. in the neck.

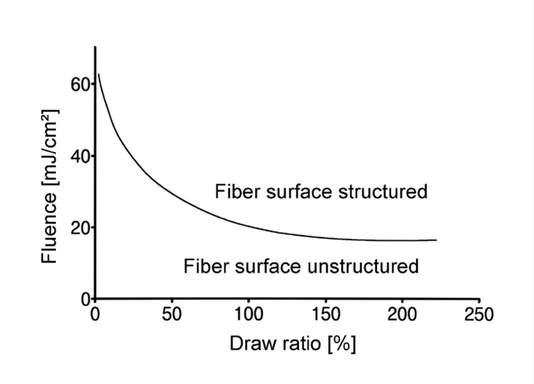

Figure 5 Threshold behavior in the formation of microstructures following UV excimer laser irradiation on fibers made of a polyurethane elastomer (Du Pont Lycra©) [7]. The topographic modification occurs only when both fluence and draw ratio exceed the values represented by the curve given in the graph.

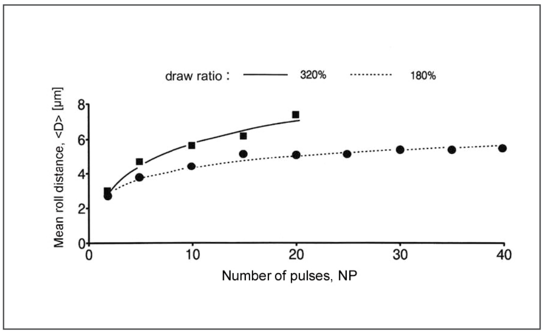

Figure 6 Mean roll distance <D> of differently drawn PET fibers as a function of the number of applied laser pulses.

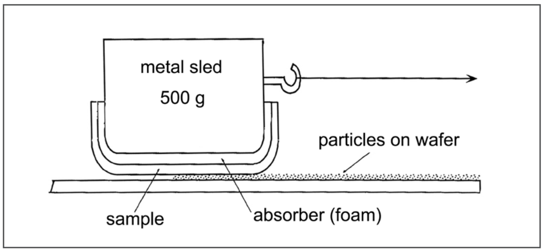

Figure 7 Experimental setup for the wiping test (see text for details).

one needs to consider the fundamental forces controlling the adhesion between (micrometer-sized) particles and the fiber surface. While van der Waals interaction, electrostatic forces and H-bonding forces determine the particle adhesion in air, i.e. in dust filtration, van der Waals forces may be regarded as the main contribution in a liquid system. For a spherical particle of diameter d on a flat surface, the van der Waals adhesion force FvdW of the particle is given by

$$F_{vdW} = \{A/12 \bullet z^2\} \bullet d$$

according to Hamaker [9]. Here, z denotes the distance between the particle and the surface (at contact z = 0.4 nm) and A the Hamaker constant. The following conclusions may thus be drawn:

- Large particles adhere strongly to smooth surfaces ($F_{vdW} \sim d$), while the contact area and, accordingly, F_{vdW} will decrease in the case of micro-rough surfaces.

- Small particles experience more contact area following roughening of the surface and, accordingly, an increase in F_{vdW} .

This shows that the UV laser treatment has the potential to increase the selectivity of a textile filter, i.e. separation of specific particle sizes as compared to others.

Dust filtration

Similar results were found in studies in industrial filter facilities with regard to dust filtration. Again, SEM investigation of dust loaded filters (fabrics and non-woven) revealed that particles were captured in the grooves of the characteristic surface structure, where much higher adhesion forces than can be expected on a smooth fiber surface acted. The quantitative measurements showed that, for the untreated filter, the filtration efficiency for particles in the sub-micrometer range was low in the new-state and increased only after longer conditioning to allow the build-up of a so-called 'filter-cake' (Figure 10). In comparison, the laser treated filter – with a mean roll distance <D> on the fibers of 2.5 µm - showed a good separation efficiency for particles below 3 µm already from the start of its use . Thus one can expect a good performance of the modified filters in clean room technology and personal protection masks.

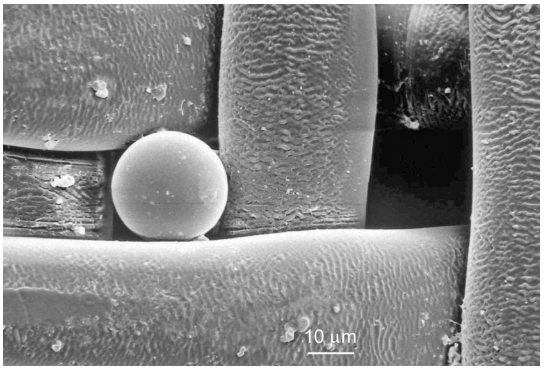

Figure 9 SEM micrograph of a textile filter – PET sieving fabric with a (mean) mesh opening of 10 µm – after wet-filtration process.

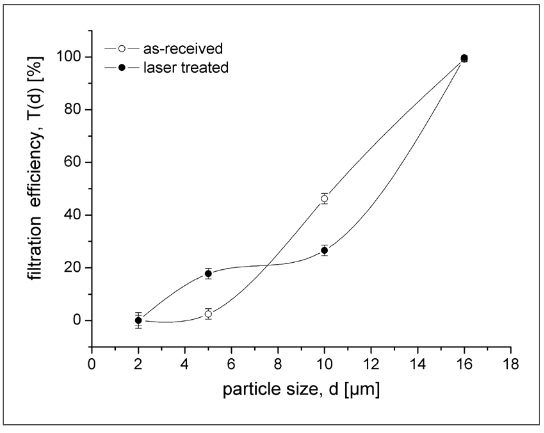

Figure 8 Mean wet-filtration efficiency T(d) of laser treated and as-received sieving fabrics in the particle size range from 2 to 16 µm (irradiation at 248 nm, 10 pulses at a fluence of 70 mJ/cm² each).

Particle removal in chip manufacturing

The effect of the laser induced micro-roughness on the wiping efficiency of PET fabrics was studied using the apparatus sketched in Figure 7, which allowed a well-defined wiping procedure. Two different fabrics (knitted PET fabrics), which basically were standard products of CLEAR & CLEAN GmbH of Lübeck, Germany, as used for applications, e.g., in microchip manufacturing, were laser modified and tested. The wiping efficiency was measured for particles of 0.2, 0.5 and 1.2 µm diameters.

A summary of the experimental data is given in Table 2. The data clearly indicate an extremely high effect for particles smaller than 1 µm where the wiping efficiency is increased by a factor of 3 and reaches more than 90 %. The data do not indicate an effect of the conditions of the laser treatment; the more intense treatment – which at least theoretically should give a more pronounced topography – giving no further increase of the wiping efficiency.

Summary

Following UV laser irradiation, the originally smooth surface of PET fibers changes to a rather regular roll-like structure on the micrometer scale perpendicular to the fiber axis.

Studies of wet-filtration efficiency as well as dust separation in industrial filter facilities revealed that particle capture, especially in the micrometer-range, could be enhanced by the characteristic surface topography created by the UV laser treatment of PET fibers. In all investigated cases, the measured separation curves showed significant increases in filtration efficiency for small particles. SEM analyses of the filters revealed that a large amount of very fine grain, i.e. sub-micrometer dust particles, was captured, which normally would not be captured on the smooth fiber surfaces of commercial filters. Accordingly, the separation efficiency is increased for small particles with the additional possibility for a specific selectivity, i.e. efficient separation of a specific particle size.

Based on this same effect of the laser treatment on particle adhesion, a modified wiping cloth showed a remarkable increase in its wiping efficiency [10].

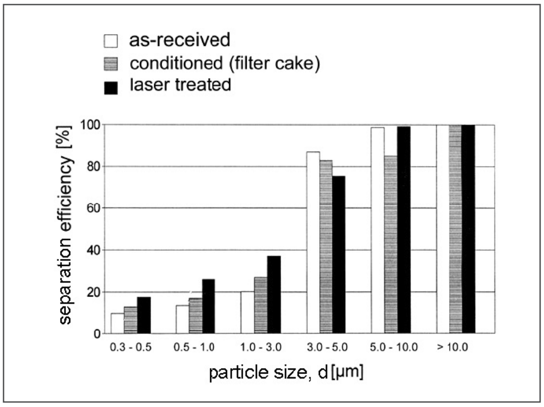

Figure 10 Separation efficiency vs. particle size of textile filters in industrial dust filtration (cotton mill). The samples studied were as-received filter, conditioned filter – i.e. as-received filter used for several days before measurement – and laser treated filter.

It may be concluded that much higher adhesion forces act in the grooves of the roll-like surface structure than can be expected from a smooth fiber surface.

Acknowledgement

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Yarn	Laser treatment	Wiping efficiency [%]		
		0.2 µm	0.5 µm	1.2 µm
50 f 88	None	32.3	31.3	99.1
	15 Pulses, 160 mJ/cm²	96.2	92.1	99.1
	20 Pulses, 200 mJ/cm²	93.7	92.3	99.1
60 f 30	None	-	20.7	-
	15 Pulses, 160 mJ/cm²	-	70.0	-
	20 Pulses, 200 mJ/cm²	-	75.5	-

Table 2 Wiping efficiency of two different wiping fabrics with and without laser treatment for particles of 0.2, 0.5 and 1.2 µm diameters. The fabrics had identical knit geometry, but were made of two different PET yarns as indicated in the Table. The two different laser treatments produced surface structures, both of which had a mean roll distance <D> of 2.0 µm, but varied in the RMS roughness.

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