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Material modification of reinforced glass fibers using pulsed laser radiation

Niels Schilling[a]*, Benjamin Krupop[a], James Bovatsek[b], Scott White[b], Rajesh Patel[b], Udo Klotzbach[a]

[a]*Fraunhofer Institut for Material and Beam Technology IWS, 01277 Dresdem, Germany*
[b]*Spectra-Physics, 3635 Peterson Way, Santa Clara, CA 95054, USA*

Abstract

In this paper, laser processing of glass fiber reinforced thermoplastics is investigated with different laser sources. The aim of the study is to determine process windows in which uniform selective ablation of polymer matrix and homogenous ablation of matrix and fiber occurs. Laser sources with different wavelengths (10600 nm, 1064 nm and 355 nm) and pulse durations in µs and ns regime are compared on their ablation behavior of natural and black colored glass fiber reinforced polypropylene. Further the effect of laser processing on the fiber strength is investigated for different parameter settings where selective ablation of polymer matrix was achieved.

Keywords: glass fiber reinforced thermoplastics, selctive laser material removal, fiber strength, joining interface, polymer filler

1. Introduction

Fiber reinforced plastics, especially long-fiber types, offer a high lightweight construction potential for many applications. 60% of long fiber reinforced materials are used in the transportation market in manufacturing of vehicles and wagons. 13% are used by sports and leisure industry and 12% by mechanical engineering industry [Lucintel, 2009]. All three market segments require large quantities of parts to be produced in a cost efficient way. Looking at the cost to benefit ratio, glass fibers in many cases have a

* Corresponding author. Tel.: +49-351-83391-3436; fax: +49-351-83391-3300.
E-mail address: Niels.Schilling@iws.fraunhofer.de.

greater benefit compared to carbon fibers, where the material production costs are still high. Because of this carbon fibers are used selectively, and in many volume applications glass reinforced thermoplastics are the material of choice.

To achieve additional cost savings long fiber reinforced material should be used only for the load bearing structures, while for other, less stressed structures, short fiber reinforced or unreinforced material can be used. Such a combination is called hybrid structure. The production of such hybrid structure begins with an endless reinforced organic sheet. Depending on the load requirements of the components and the stress direction, layers with different fiber directions can then be combined and consolidated [Firotto, 2013]. Shaping of additional reinforced and unreinforced structural elements like ribs can be done with inkjet molding.

One of the issues in forming geometrical shapes is the interface between the organic sheet structure and additional shaped structures. During the production process a stress transmission path from the unreinforced elements to the long fiber reinforced part must be generated. One approach to get this is to heat the organic sheet and injected material up to the decomposition temperature of both. Because of low viscosity a good intermixing at the interface is achieved. But this approach requires a good ability to control the temperature. Too much heat energy leads to local degradation of the polymer and bad interfaces where the connection is held together mainly by surface adhesion. In this case the shear strength at the interface is reduced [Firotto, 2013]. Research is underway to overcome such weak points by generating contact areas. For one such process the polymer rich surface layer has to be removed completely and further a small layer of reinforcing fibers has to be selectively freed from surrounding polymer by selective laser ablation with a minimum of damage at the reinforcing fibers. This contact point is then filled with new polymeric matrix material by inkjet molding technique. In this paper results of selective and matrix ablation and homogenous ablation with pulsed lasers and its effect on the fiber strength is presented.

2. Material and Methods

2.1. Sample Material

The research on selective matrix removal was done using black and natural colored polypropylene samples with unidirectional (UD) and woven glass fibers. The natural colored substrates are produced out of hybrid yarn with a fiber volume content of 60 vol% [Golzar, 2007]. The black colored UD material is produced out of “Plytron” sheets from Elekon with a fiber volume content of 35%. The second black substrate specimen was made out of woven Twintex TPP 60 also with a fiber volume content of 35%. The black color in both cases is due to carbon black (CB) used as filler, specific content of CB is not known. For overcoming this behavior a study on the ablation threshold and the ablation rate was done at probes with 1 wt%, 2 wt% and 3 wt% content of carbon black.

For laser processing the transmission properties of the material determines the appropriate laser systems to use. In Fig. 1 the absorption curve of natural Polypropylene (PP) is shown. The estimated reflection, when calculating over the refraction index change, is 4 %. It can be seen that over a wide wavelength range nearly 90% of the radiation transmits through the material. The additive carbon black in the colored samples is a broadband absorber and can increase the absorption, depending on the content. A content of around 1-3 % by mass leads to transmission values near zero for a large range of wavelengths.

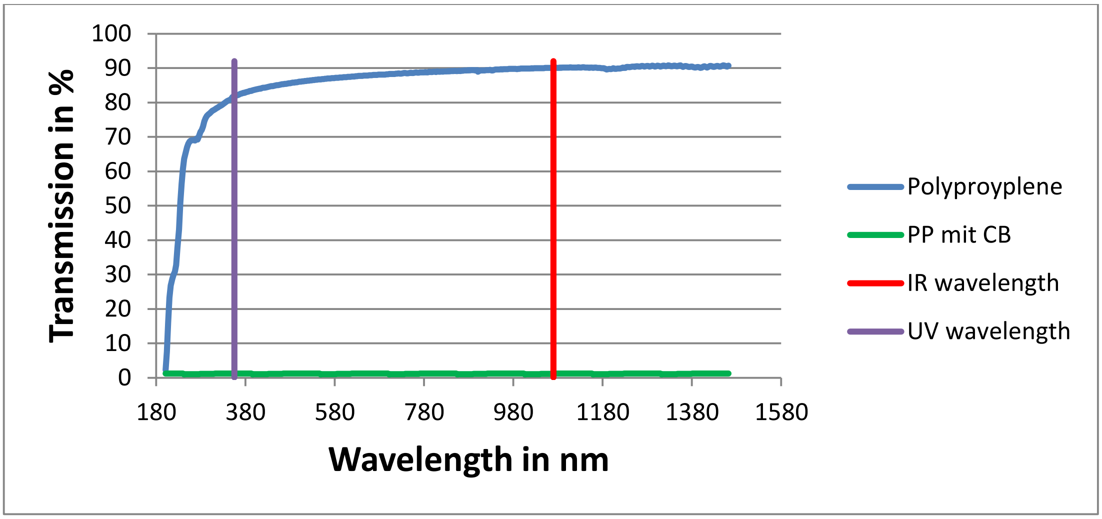

Fig. 1: Transmission of polypropylene in the range of 200 nm up to 1580 nm.

In this study the focus was set on laser wavelengths and systems which are relevant for industrial polymer processing. In detail this means the wavelength 10600 nm from CO_2 laser which is still relevant for industrial processing. Further a laser system in the NIR is chosen, which can be used when filler material is added to the polymer, and an industrial ultraviolet (UV) – system with a wavelength of 355 nm was tested. The CO_2 laser wavelength is the only one which shows strong absorption for natural PP. The drawback for the CO_2 laser and the UV laser, to a lesser extent, is that glass also shows absorption at these wavelengths.

2.2. Laser systems

Based on the material properties three different pulsed laser sources where chosen for the study. As established laser system for polymer ablation a modulated CO_2 laser SCx 20 (Rofin Sinar, Germany) was used with up to 200W and a pulse duration of maximum 400 µs. Second was a ns - fiber laser YLP-1 (IPG Photonics Corporation, USA) with 20 W average Power and a pulse duration of 100 ns. Finally the high power UV Quasar® 355 nm 60W laser from Spectra-Physics® was used in the experiments, which is shown in Fig.2.

Fig. 2: A high power 355-nm UV Quasar® laser used in the experiments

The Quasar produces >60 W of power at 300 kHz and is capable of producing pulse width varying from <2 ns to >100 ns and repetition rate from single shot to 3.5 MHz. It is also the first laser of this class to offer TimeShift™ technology, enabling pulse energy programmability in the time domain and pulse width variation, as well as pulse splitting and burst mode operation. By splitting the pulses at a given repetition rate, the material can dissipate heat and/or plasma such that more efficient material removal is expected. By altering the number, spacing, and relative intensity of pulses within a burst, the spatial-temporal thermal profile in the work piece can be tailored for speed and quality of machining. The laser parameters of all lasers are shown in table 1.

Table 1. Parameter overview of the used laser systems

Laser system	SCx20	YLP-1	Quasar
Wavelength	10600 nm	1070 nm	355 nm
Average Power	200 W	20 W	60 W
Repetition Rate	0 – 100 kHz	20 – 100 kHz	Single shot – 3.5 MHz
Pulse duration	<400 µs	100 ns	2 ns - >100 ns
max. pulse energy	190 mJ	1 mJ	300 µJ
Focal length	200 mm	163 mm	163 mm
Spot diameter	450 µm	80 µm	24 µm

2.3. Methods

The first goal of the research was determination of the laser ablation threshold of the pure materials used in the composite. This was done by the approach described by Mannion, 2003. For the Spectra-Physics UV - laser and the RS CO_2 – laser the polymer matrix and the reinforcing glass fibers need to be tested because both material show significant absorption for the radiation. For the same reason for IPG IR ns laser only the polymeric matrix with filler has to be tested on the ablation behavior. The reinforcing fibers should not show any ablation effect at the working parameter of the laser system. Starting from the material threshold values a parameter matrix consisting of pulse energy, pulse overlap and number of repetitions were applied at the different material samples of unreinforced and reinforced substrates. The optical characterization was done with a VHX-100 (Keyence Deutschland GmbH, Germany). For the unreinforced substrates the ablation depth is measured by conventional depth gauge and a confocal microscope Leica DCM (Leica Microsystems GmbH, Germany).

Second goal was to investigate the effect of different laser parameters on the strength of the reinforcing fibers. The process of selective matrix removal can only be done in a region near the surface within a thickness of about 100 µm. The testing method used for unidirectional fiber reinforced materials is described in DIN EN ISO 527-5. In this specification the material thickness of probes is given with one and two millimeters. So the influence of the processed surface layer on the resulting tensile strength of the specimen can be neglected. To overcome this, probes have been cut out of the “Plytron” sheet material with a geometry based on the DIN EN ISO 527-3, which is mainly used for polymer foils with a thickness below 1 mm. The given geometry has been cut out by CO_2 – laser. In the testing area of the tensile probe the polymer matrix is removed by the identified usable laser parameters. The scan direction of the laser was always perpendicular to the fiber direction.

3. Results and Discussion

3.1. CO_2 - laser processing

For the working wavelength 10600 nm the ablation threshold of the PP matrix with and without carbon black was investigated. The ablation threshold for the natural PP was determined with 2.67 J/cm². The probes with 1wt% and 2 wt% carbon black the threshold values were determined with 2.60 J/cm² and 2.64 J/cm² which is very close to the value of natural PP. This shows a low influence of CB on the resulting ablation threshold and indicates that the ablation behavior is mainly given by the polymer. The ablation threshold for the glass fibers is determined with 3.45 J/cm². Compared to the value of the polymer matrix only a small process window where a selective ablation seems to be possible.

After validating all relevant material parameter the parameter matrix was realized for 1, 2.4, 3.65, 7.5 and 10.5 mJ. The pulse overlapping was varied from 0, 25, 50, and 75 % of the spot diameter and number of repetitions from one, two, and five cycles.

Table 2: Parameter combinations of CO_2 laser processing where a selective matrix ablation can be shown at one repetition. More repetitions lead to high fibre damage.
O=selective Ablation, x= homogenous ablation, /=only local interaction with the polymer matrix

Pulse energy in mJ	0 % overlap	25 % overlap	50 % overlap	75 % overlap
1	/	/	/	/
2.4	/	/	O	X
3.65	/	O	X	X
7.5	/	X	X	X
10.5	/	X	X	X

Only two combinations at low pulse energy and low overlap showed acceptable results with minimal thermal influence of the reinforcing fibers. At higher overlap and pulse energies the reinforcing glass fiber was thermally damaged or completely molten. In Fig 3 the fiber behavior of processed probes is shown.

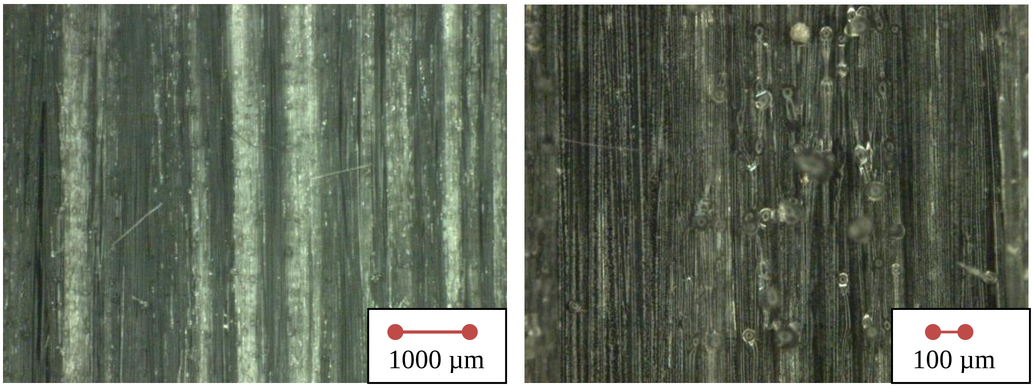

Fig. 3: Overview (left) and detail view (right) on CO_2 processed strength probes. In the detail view local fusion points and the forming of glass pearls along the fibres can be observed

These two parameters were applied at tensile probes to evaluate the effect on the fiber strength. The testing shows a strength reduction of 41% from 473.6 MPa to 278.5 MPa for both parameter combinations.

One possible explanation for this change can be given through the behavior that only local fiber damaging happens at these two parameters and the testing method given represents the maximum achievable fiber strength.

3.2. IR - ns laser processing

At a working wavelength of 1070 nm, minimal absorption occurs in the natural PP matrix (90 % transmittance, see Fig. 1) and in the reinforcing glass fiber. Thus the investigation has been done only for probes with carbon black content. The ablation threshold for 1 wt% CB is 0.801 J/cm² and for 2 wt% 0.533 J/cm². The decrease in the material threshold can be explained by a change in the absorption behavior from volume absorption to shallow surface absorption [Acherjee, 2012]. Through this change, the peak temperature in the radiated layer increases which leads to a decreasing material threshold for laser ablation. The determination of the ablation rate at different fluences and pulse overlaps shows strongly a combined process characteristic of material melting, vaporization and sublimation which is caused by the carbon black filler. In the center of the laser spot the polymer material was sublimated because of high fluences. In the outer regions of the laser spot, vaporization occurred where the accumulated energy was sufficiently high, and outside this region the material was melted. An explanation of this behavior can be given by the fact that the energy input in the polymer material happens indirectly over sublimating/heating of the graphite. With a specific time delay the temperature of the polymer rises after the interaction of the laser pulse [Lee, 1992; Wen, 1994]. This behavior occurs inside and outside the radiated spot area depending on the local fluence. When structuring an area with overlapping pulses this behavior causes a strong material melting and re-melting which causes an inhomogeneous material flow and makes a measurement of the ablation rate difficult. As a result of this behavior , a test matrix was implemented where the fluence was varied between 0.23 J/cm² and 11.24 J/cm² and the pulse overlap was varied from 0 % to 75 % with a step width of 25 %.

Table 3: Parameter combinations for IR ns –laser processing. / = local modification, O = selective ablation, X = fibre damage

Fluence in J/cm²	0 % overlap	25 % overlap	50 % overlap	75 % overlap
0.23	/	/	/	/
1.41	/	/	/	O
2.75	/	/	/	O
4.17	/	/	O	O
5.58	/	/	O	X
6.99	/	O	O	X
8.49	/	O	O	X
12.24	O	O	O	X

In Table 3 it can be seen that selective material removal of the polymeric matrix can be realized over a wide range of parameter combinations. The microscopic characterization in Fig. 4 shows a polymer film at the reinforcing fibers whose amount strongly correlates with the processing parameters. At higher fluences and pulse overlaps the thickness of this film decreased. The microscope inspection showed also local parts of the fibers which are completely cleared from the matrix. Working with higher fluences than 5.58 J/cm² at high overlaps can lead to local damages of the reinforcing fibers. This damage is caused through thrust loading of the glass fibers which is caused by vapor pressure generated from matrix vaporization of deeper composite regions.

The strength testing was done for three different parameter sets. First was 50% overlap at a fluency of 6.99 J/cm² and second at 12.24 J/cm². The third parameter combination was 93% overlap at 1.41 J/cm². With this high overlap the matrix removal out of the testing area is done over simple material heating and melting. The transport direction of the material depends on the scan direction. The optical behavior of these three conditions is shown in Fig. 4 and the testing results in Table 4.

Fig. 4: Behaviour of selective matrix removal at a. Parameter set 1 with 6.99 J/cm² and 50 % overlap, b. 12.24 J/cm² and 50 % overlap and c. 1.41 J/cm² at 93 % overlap. In a. some of the fibres are still embedded in the polymer matrix. In b only a small polymer film left around the fibres and fibre damaging can be observed. In c the fibres are completely freed from polymer

Table 4: Testing results on maximum achieved fibre strength and modulus of elasticity for the three parameter sets.

Condition	Strength in MPa	Reduction on	Modulus of elasticity in GPa	Reduction on
Untreated	473.6		24.5	
Parameter set 1	295.5	62 %	22.7	93 %
Parameter set 2	91.4	19 %	19.5	80 %
Parameter set 3	206.6	44 %	23.6	96 %

3.3. UV - ns laser processing

The UV Quasar laser is the third laser system used in the study to process both types of reinforced PP. The CB content, as mentioned above, acts as a broadband absorber over the whole spectra shown in Fig. 1. The processing without CB works with an expected absorption of around 14 % to 16 %. With this situation the laser irradiation is absorbed in a larger material volume. This leads to a material removal characteristic given by heating, melting and vaporization and not sublimation which is the general removal mechanism when working with short pulsed lasers and having high absorption coefficients. Through the TimeShift™ function of the Quasar laser different pulse durations were used for material processing. In this study the focus was set on 2 ns pulse duration to realize minimal interaction time and 30 ns to compare the results achieved with other commonly available UV laser systems. Quasar's TimeShift technology can also generate more unusual pulse outputs—such as shaped pulses and pulse bursts—which are not available with any other UV laser source, and it was used to generate preliminary threshold and removal rate data with a burst of 5 pulses with 2-ns pulse duration.

For the reinforced natural polypropylene probe the threshold was 2.85 J/cm² for 2 ns pulse duration and 6.61 J/cm² for 30 ns pulse durations. The CB filler led to a higher absorption of the UV-radiation and hence a reduced ablation threshold. For 2 ns pulse duration the threshold was determined to be 0.81 J/cm² and for 30 ns it was 1.63 J/cm², which means a reduction of ~3x or higher for both pulse durations with the CB filler. In the case of 5x2ns burst machining, the thresholds for unfilled and CB-filled materials were 6.1 and

1.02 J/cm², respectively. For consideration of the individual pulses within the burst, these figures should be divided by five, which yields 1.22 and 0.2 J/cm², respectively. These numbers are significantly lower than the corresponding figures for single 2-ns irradiation, indicating the occurrence of threshold reduction by way of electronic and or thermal incubation. For both tested materials a strong melting and re-melting can be observed when looking at the material removal behavior. For the unfilled PP this comes from the volume absorption of the UV radiation. For the CB filled material it is the same mechanism as described in section 3.2 for the IPG laser.

For both materials it is necessary to find an optimum for sufficient material melting which can be used in a defined way to free the fibers from the polymeric matrix. In Fig. 5 different stages of processing in relation to the overlap is shown. When working with high pulse overlap of 75% a behavior can be observed at which the fibers at the processing surface were surrounded again by polymer matrix. Additional blowholes with a thin polymer layer can be observed. This is caused through a strong material vaporization effect below the surface and in deeper material regions which cause a statistical reclosing of the reinforcing fibers.

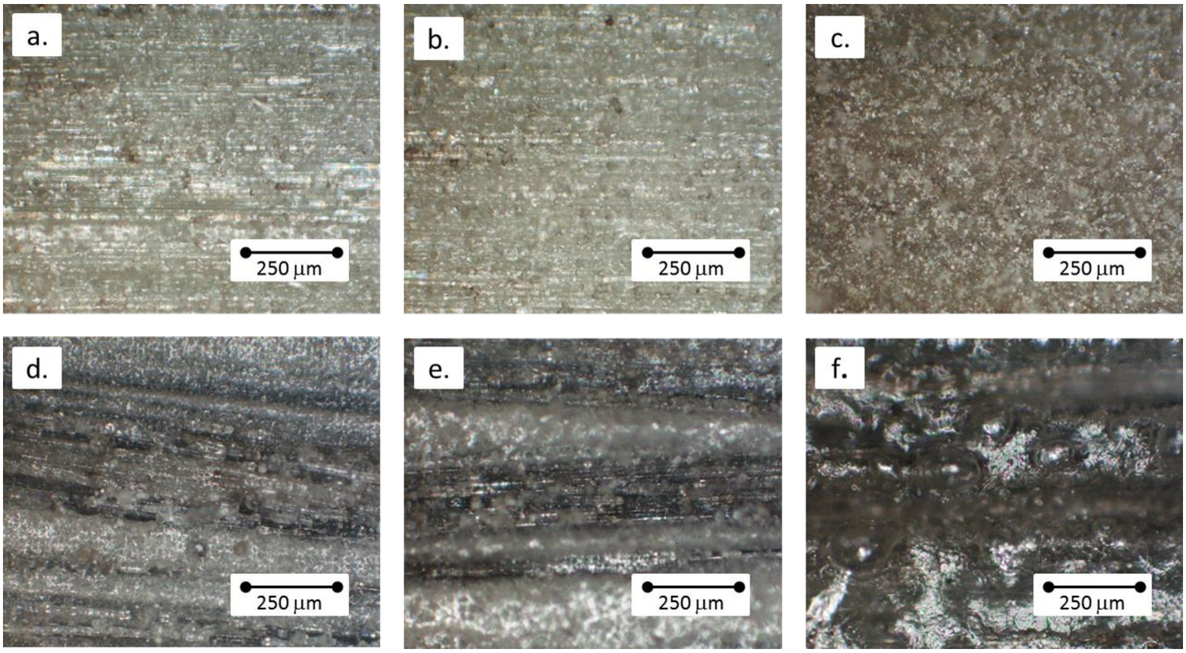

Figure 5: Appearance of freed fibres from surrounding polymer matrix for natural PP (a, b, c) and CB filled PP (d, e, f) processed with 2 ns pulse duration and with rising overlap from 25 % (a, d) to 50 % overlap (b, e) and 75 % overlap (c, f)

Based on the preliminary investigation a parameter matrix was applied for the reinforced material where the overlap was varied between 25%, 50% and 75% and fluency was varied in multiples of the material ablation threshold. The results on processing the reinforced material under the aspect of freeing the fibers from surrounding matrix material are represented in Table 5.

Table 5: Overview of all tested parameters for UV Quasar laser processing of the natural and the CB filled PP probes. / = local modification, O = selective removal, X = strong melting

Material	Fluence in J/cm²		25 % overlap	50 % overlap	75 % overlap
	2 ns pulse duration	30 ns pulse duration			
natural PP	2,8	6,1	/	/	/
	5,7	12,2	O	O	O
	8,5	18,3	O	O	O
	11,4	24,4	O	O	X
CB filled PP	0,8	1,6	/	/	/
	1,6	3,3	/	/	/
	2,4	4,9	O	O	O
	3,3	6,5	O	O	O
	4,1	8,1	O	O	X

All results were achieved with one or two repetitions per area. Increasing the fluence and the number of repetitions led to a defined material removal of reinforcing fibers and polymeric matrix. Such behavior is important to understand when addressing additional applications in the field of reinforced plastics like generating contact points for integrated devices such as sensors or actuators. In Table 6, a short overview of achieved material removal rates per pulse at different parameters is shown. The fiber strength testing of UV laser processed sample is underway and we will report data shortly in future.

Table 6: Overview of material removal rates per pulse

Material	Pulse duration in ns	Fluency in J/cm²	Material removal in µm/pulse
Natural PP	2 ns	11,4	4,64
	30 ns	12,2	1,97
	30 ns	24,4	5,77
	5x2 ns	18,3	9.94
CB filled PP	2 ns	123,1	14,26
	30 ns	6,5	27,96
	5x2 ns	16,32	13,58

4. Conclusion

In this study the processing of glass fiber reinforced polypropylene was studied. For this two kinds of material removal were identified. First is the selective matrix removal where the reinforcing fibers are freed from the surrounding polymer. Best results for this behavior were achieved for CB filled material with an IR-laser. It was possible to free fibers in a depth of approximately 200 µm. However, IR laser does not work well for natural PP. For natural PP, the Quasar UV laser shows best results in the case of selective matrix removal. With the Quasar UV laser it was possible to free the fibers locally in the depth of 10 µm which is the diameter of the reinforcing fibers. Quasar UV laser also works very good for selective removal of CB filled PP matrix in combination with high achievable machining speed.

In case of homogenous removal of polymer and glass fibers, best results were achieved with the Quasar UV laser for both natural and CB filled PP. The combination of high material removal rate and high available repetition rate in MHz regime also offers the possibility for high throughput processing for cutting and drilling in the same way and with the same laser as used for fine processing for generating contact points at integrated structures. It was also observed that operating the Quasar with a burst pulse output consisting of 5x2 ns pulses resulted in reduced ablation thresholds and in some cases enhanced material removal rates, further demonstrating the processing flexibility offered by Quasar laser. A summary of results achieved using different laser for natural PP and CB filled PP is tabulated in table 7.

Table 7. Summary of results achieved using different lasers for natural PP and CB PP material

		Selective ablation of matrix		Homogeneous ablation of matrix + fiber	
	Wavelength	Natural PP	CB filled PP	Natural PP	CB filled PP
CO2-Laser (RS SCx20)	10600 nm	X (small process window)	X (small process window)	✓ (high thermal damage)	✓ (high thermal damage)
IR- Laser (IPG, YLP-1)	1070 nm	X (no process window)	✓✓ (good Quality)	X (no process window)	✓ (indirect fiber damage)
UV-laser (SP, Quasar)	355 nm	✓✓ (large process window)	✓✓ (good quality and speed)	✓✓ (large process window)	✓✓ (good quality and speed)

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