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Laser surface modification of structural glass for anti-slip applications

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Abstract:

The use of soda-lime silicate glass as a structural element has become frequent in modern buildings. The load-bearing applications of glass in floors, footbridges, terraces, or stairs require an optimal combination of non-slippery properties of the surface, element weight, and strength, and structural glazing can be compromised by the incorporation of laser surface patterned ornamental motifs. Laser surface modification has significant advantages for selective surface area modification; nevertheless, the mechanical performance of the processed glass remains unknown, which precludes reliable structural calculations and employment in construction. In this study, we investigated the surface modification of annealed and heat-strengthened glass via CO_2 laser scanning for the production of rough anti-slip surfaces. The surface roughness and the reduction of the bearing load strength were quantified. Slip resistance-enhanced surfaces with roughness values (Rz) above 20 μm and characteristic bending strength preservation up to 74% were obtained. The results pave the way for the use of laser surface-modified plates in laminated glass elements with optimized strength calculation and weight reduction.

Keywords: structural glass; heat strengthened glass; CO_2 laser; surface treatment

Article outline:

1. Introduction

The use of glass in architecture has increased during the recent decades owing to its transparency, durability, and availability. Currently, no modern building is conceived without the use of glass, and its application as a secondary structural element has become frequent. In 2017, more than 10 million tonnes of flat glass was produced in Europe, approximately 70% of which was float glass for the building industry [1]. In glass load-bearing applications such as floors, steps, and glass barriers, the risk of damage due to element failure is elevated, and high levels of structural safety and reliability are demanded [2,3]. Slipperiness is involved in 40%-50% of the fall accidents, and slips -the worldwide leading cause of non-fatal injuries- have important health and economic impacts [4–8]. Thus, the horizontal glazing on floors, footbridges, terraces, and stairs requires slip-resistant surfaces to prevent falls in presence of contaminants. Nevertheless, the modification of the upper surface of these elements involves the alteration of the glass strength due to the induction of stress concentration and additional crack nucleation points. For instance, the use of patterned glass frequently implies a 55% reduction of the annealed glass expected strength, as well as the inclusion of a surface profile factor that reduces the calculated design value by 25% [9–11]. Moreover, in some modern applications of glass laminates, such as glass elements in cruise vessels, weight reduction is a matter of great significance, and oversizing must be avoided [12]. To perform accurate structural calculations and to implement the structural failsafe concept in glass elements, with an optimal combination of the slip resistance, weight, and element strength, it is necessary to determine the impact of surface processing on the mechanical properties [2,13].

Current surface processing methods considered by structural glass standards include mechanical polishing, grinding, etching, and sandblasting. However, these procedures have significant limitations, such as long processing times, the use of dangerous substances, low surface-area selectivity, required mechanical contact, the production of dust, and a noisy working environment [14,15]. Among the different techniques for material surface roughening and texturing, laser surface modification has potential advantages as a non-contact method for selective surface area treatment [16–18]. The use of a femtosecond pulsed laser was reported for the production of microholes on fused silica glass surfaces, and for the texturing of superhydrophobic surfaces on soda-lime silica glass [19–21]. The use of an excimer laser combined with phase masks was reported for the surface structuring of silica glass fibre [22]. Nevertheless, the mechanical performance of the laser-processed glass remains unknown, precluding reliable structural calculations and its employment in construction structural elements.

In this study, we investigated the surface modification and characterization of annealed and heat-strengthened soda-lime silica glass via CO_2 laser scanning for the production of rough anti-slip surfaces. Although early research on the application of the CO_2 laser to silicate glass was limited by the laser source optical power [23], among the different laser sources, the use of the mid-infrared wavelength is particularly interesting owing to its high absorption by silicate glass and the currently available high optical power sources [24–28]. This processing technique employs a laser beam, which is focused on and used to scan the glass surface, with a controlled scanning speed in an air atmosphere for modifying the surface topography and confering specific properties. The obtained results with regard to the surface roughening and mechanical strength pave the way for the use of laser surface-modified plates in laminated glass elements that require slip-resistant surfaces, with optimized strength calculation and weight reduction.

2. Materials and Methods

2.1. Materials

The composition of the soda-lime silicate (SLS) glass employed in this study was as follows (wt. %): 72.6 SiO_2, 13.9 Na_2O, 8.4 CaO, 4.3 MgO, 1.1 Al_2O_3, 0.6 K_2O, 0.2 SO_3, 0.11 Fe_2O_3. Heat-strengthened and annealed float glass plates with a thickness of 4 mm were employed for laser surface modification experiments. The surface of the unprocessed samples exhibited an arithmetic average roughness of Ra = 0.024 µm and an average roughness depth of Rz = 0.17 µm.

2.2. Laser surface treatment

The laser treatment was performed using a 3.5-kW CO_2 slab laser (Rofin-Sinar DC035, Hamburg, Germany), emitting a TEM_{00} laser beam at a 10600-nm wavelength. The laser beam was focused onto the surface of the sample using a 710-mm focal length lens coupled to a polygonal rotating mirror. The achieved processing area of 220 mm × 0.56 mm was scanned to perform a wide surface treatment by using a computer numerically controlled table. The laser surface treatment was performed in air at the atmospheric pressure. The laser was operated in the continuous-wave (CW) mode with a constant laser optical power of 300 W, at scanning speeds between 50 mm/min (energy density of 1.64 J/mm^2) and 600 mm/min (energy density of 0.14 J/mm^2). Laser surface modification with pulsed mode operation (pulse repetition rate of 3000 Hz) was performed in preliminary tests to compare the obtained surfaces.

2.3. Sample characterization

The surface roughness of the processed samples was measured using a stylus profiler (Taylor-Hobson Form Talysurf Plus) in accordance with the international standard ISO 4288:1996. The profiler was set to employ a Gaussian filter corrected in phase with a cutoff of 2.5 mm. The specified surface roughness values corresponded to the arithmetic average roughness (Ra) and average roughness depth (Rz). The reference line for average roughness calculation was selected to set identical areas below and above the line. The surface roughness of the laser-processed samples was measured along directions parallel and perpendicular to the scanning direction. The processed surface was carbon coated and examined via scanning electron microscopy (SEM, Philips XL-30) with an accelerating voltage of 10 kV.

Measurements of the contact angle using bi-distilled water were performed via the sessile drop technique to determine the wettability of the treated areas. A liquid drop was placed on the surface using a calibrated syringe. Then, the contact angle was measured using a goniometer measuring system (FIBRO System) with a minimum of 10 measurements per sample. Measurements of the slip angle were performed on completely processed surfaces under dry conditions, in water-wet and in oil-wet conditions (SAE 10W30), following DIN 51130 ramp test specifications.

Fourier transform infrared (FT-IR) spectra were acquired from the glass sample surfaces in the range of 400 and 4000 cm^{-1} (resolution of approximately 2 cm^{-1}) using an

Agilent Tech Cary 630 spectrometer coupled to a diamond attenuated total reflectance (ATR) crystal.

The Vickers microhardness was measured adjacent (100-μm fringe) to the laser-modified surface, by using a Shimadzu microhardness tester. A force of 4.903 N was applied over 18 s. Inmediately after indentation, the fracture toughness K_{Ic} and fracture surface energy γf were evaluated, from the well-developed radial cracks according to the method established by Anstis and Miyoshi [29,30]. Values of 72 GPa and 0.23 were employed for the Young's modulus and Poisson's ratio, respectively [31–35].

The four-point bending strength of glass plates having lateral dimensions of 250 mm × 60 mm and a thickness 4 mm, with a 250 mm × 25 mm laser-modified surface, was determined in accordance with ASTM c158 standard. The sample edges were carefully grinded and polished. For each condition, tests were repeated 15 times using a Walter-Bai axial testing machine equipped with a 25-kN load cell.

3. Results and Discussion

Figures 1.a and 1.b show the appearance of the modified SLS glass surface after CW laser processing and pulse-mode laser processing, respectively. The SEM observation of the modified SLS glass surface after CW laser processing (Figure 1.c) shows that the glass removal is produced in fragments of hundreds of microns. The curved surfaces intersect at the peaks and valleys of the glass surface topography. In addition to aesthetic differences, the surfaces processed by pulsed-mode laser retained a large amount of stuck glass microparticles (Figure 1.d), leading to the potential problem of abrasion. The surfaces processed in the CW mode exhibited a more directional and regular appearance; thus, in depth characterization of the samples processed by the CW laser was performed.

3.1. Surface roughness and slip angle

3.1.1. Surface roughness

Figure 2 shows representative surface profiles obtained at different scanning speeds, revealing a significant roughness variation at low scanning speeds. The measured values for the arithmetic average roughness (Ra) and average roughness depth (Rz) of the laser modified surfaces are shown, in Figure 3.a and 3.b, respectively, with respect to the scanning speed. The surface roughness decreased with the increasing scanning speed, with maximum Ra values below 15 μm and minimum Ra values above 3 μm, while the obtained Rz values were between 20 and 80 μm. The differences were more significant at low scanning speeds, and the roughness stabilized at minimum values at high scanning speeds. The measured roughness in the direction normal to the scanning direction was slightly higher than that in the direction perpendicular to the scanning direction, which was related to the directional characteristic of the one-pass scanning laser-assisted technique. While the surface roughness measurement alone is insufficient for determining the slip resistance, it indicates a clear improvement compared with the unprocessed SLS glass surface.

3.1.2. Slip angle

The ability of the SLS glass processed surfaces to increase the slip resistance was quantified via measurement of the inclination angles in oil-wet, water-wet and dry conditions. Figure 4 shows the average slip angle with respect to the laser energy density. The average slip angle in the oil-wet condition, with observed values between 29° and 34°, mainly remained constant in the range of the investigated processing conditions. The unprocessed glass surface exhibited a slip angle of 8.3 ± 1.5° in oil-wet conditions. The laser-processed surfaces were identified as low slip risk surfaces and are considered suitable for wet areas, while the bare glass surface presents a high risk and should be restricted to dry areas. Additionally, the laser modification improved the slip resistance in the water-wet conditions and in dry conditions. The unprocessed glass surface showed a slip angle of 13.6 ± 1.0° and 25.6 ± 0.9° in the water-wet and dry conditions, respectively. Therefore, according to the inclination angle and surface roughness observations, the surface modified by laser scanning can be considered as a slip resistance-improved surface. These precise quantitative results should be taken with caution given the diversity of floor slip resistance characterization techniques [36,37].

3.2. Surface hardness and fracture toughness

To assess the effect of the laser energy on the glass samples during the surface modification process, the surface hardness was measured on the proximal surface to the laser modified band. Table 1 presents the average values of the hardness, fracture toughness and fracture surface energy of the annealed SLS glass for different scanning speeds. The hardness of the as-received glass was mainly maintained after the processing, even for conditions of a low scanning speed and high energy input. A reduced-hardness zone in the proximity of the laser modified surface was not observed.

The fracture toughness and fracture surface energy were assessed from the radial cracks immediately after indentation [29,30] (Figure 5), and the obtained values for the annealed SLS glass are presented in Table 1. The hardness values measured from microindentation did not exhibit significant modifications and remained within the reported values for SLS glasses with similar compositions [38–40]. In contrast, the observed fracture toughness and fracture surface energy deviated slightly from those of the original annealed glass. The fracture toughness decreased as the scanning speed was reduced; therefore, it decreased as the linear energy density increased. For laser energy densities lower than 0.27 J/mm^2 (scanning speed values greater than 300 mm/min), the toughness reached the values of the original glass. This effect is clearly observed in Figure 6, which shows the fracture toughness with respect to the linear energy density. The observed K_{Ic} values for the reference annealed glass agreed well with the values reported for SLS annealed glasses [34, 41–45].

The hardness, fracture toughness and fracture surface energy of the heat-strengthened SLS glass after laser processing are presented in Table 2. The values indicate that the heat-strengthened glass was less susceptible to a toughness reduction than the annealed SLS glass, owing to the laser surface processing. Crack propagation was prevented by the compressive stress induced during the heat treatment on the surface; hence, the obtained toughness values were increased. According to the trends of the fracture toughness and fracture surface energy with respect to the scanning speed, optimal processing conditions (scanning speed 350 mm/min and laser energy density 0.23 J/mm^2) were selected to achieve a trade-off between the anti-slip property and the predicted mechanical behaviour, while maintaining the aesthetic quality.

3.3. Contact angle

The wettability for distilled water was significantly increased after the laser surface modification. The average measured contact angle for the optimized processing conditions (300 W, 350 mm/min, 0.23 J/mm^2), was 25 ± 1°, while the contact angle for the as-received glass surface was 67 ± 2°. Figure 7 illustrates the different behaviours regarding the distilled water wettability. The measured contact angles of the surfaces modified using different processing conditions, did not exhibit significant differences within the investigated scanning speed range, with an overall average value of 21 ± 4°. Slipping on a glass floor is very likely to occur when a sufficiently thick liquid film precludes the contact between the glass surface and the footwear sole material, causing a dramatic reduction of the friction coefficient. The high affinity of the laser-modified surfaces to liquid prevents the formation of thick liquid films and reduces the potential slip danger [46].

3.4. FT-IR spectra

The ATR IR spectra obtained from the surfaces of the as-received and modified SLS glass are shown in Figure 8. The observed bands around 758 and 890 cm^{-1} are related to Si-O-Si bending and Si-O-NBO (non-bonding oxygen) stretching vibration modes, respectively, and the Si-O-Si stretching vibration mode was present as a shoulder peak around 1020 cm^{-1}. The peak position of the Si-O-Si bending mode for the thermally strengthened SLS glass exhibited a + 3 cm^{-1} shift compared with the peak position for the annealed SLS glass. This blue shift is attributed to bond angle or bond length alteration due to the modified stress state at the glass surface [47,48]. After the laser processing, the Si-O-Si bending mode peak shift for the thermally strengthened SLS glass was less clear, suggesting that the compressive constraint at the glass was partially released by the laser surface modification. The peak shift of the Si-O-NBO stretching mode, which was observed for the as-received glasses, was more difficult to locate with precision for the laser-processed samples owing to the Si-O-Si stretching shoulder peak.

3.5. Bending strength

To determine the bending strength of the surface-modified samples, annealed glass SLS plates and heat-strengthened SLS glass plates were subjected to bending tests. The experimental Weibull graph and cumulative failure probability for the as-received annealed glass are shown in Figures 9.a and 9.b, respectively, and analogue experimental charts for the laser surface-modified annealed glass are shown in Figures 9.c and 9.d, respectively. The Weibull characteristic bending strength of the annealed glass was reduced from 135 to 91 MPa owing to the laser surface modification. Additionally, the corrected Weibull modulus was modified from 4.9 to 9.5. The modification of the bending strength behaviour was clearly indicated by a comparison of the maximum values of the populations, which was reduced from 178 to 105 MPa. The observed failure stress distribution for the reference unprocessed glass agreed well with the reported failure behaviour of annealed glass [49].

The experimental Weibull graph and cumulative failure probability for the heat strengthened SLS glass are shown in Figure 10. Similar to the behaviour previously described, the laser surface modification reduced the Weibull characteristic bending strength from 165 to 122 MPa, while the corrected Weibull modulus increased from 5.5 to 10.0. The maximum value of the populations was reduced from 215 to 135 MPa. These findings provided insight regarding the mechanical performance of laser surface-modified glass, and indicated that the characteristic bending strength preservation was 67% and 74% for the annealed and heat-strengthened glass, respectively. From an application viewpoint, the effect of an increased Weibull modulus is the concentration of the expected failure stress around the characteristic strength; i.e., the surface laser processing leads to a “more reliable” failure around a lower typical value of the stress.

The consideration of a third parameter to obtain a better interpretation for the lower bound of the failure stress has been proposed, such as the lower value of the experimental population or the stress value for a 5% failure probability [2,50]. The bending strength prediction with a failure probability of 5% and a confidence interval of 95% was mainly preserved after laser surface modification. This value for the annealed SLS glass and the heat-strengthened SLS glass was 65 and 85 MPa, respectively, before the surface processing and 63 and 85 MPa, respectively, after the laser surface modification. These values are consistent with the minimum strength expected for the annealed and heat-strengthened SLS float glass [2,51] and slightly superior to those obtained via a tensile test of non-bevelled glass samples [52].

4. Conclusion

The ability of a CO_2 laser to modify the surface roughness of SLS glass was demonstrated. The effects of the scanning speed and energy density on the surface roughness were investigated, and Rz values between 20 and 80 µm were obtained. The liquid affinity of the surface was increased by the laser treatment. This influence was observed regardless of the specific processing conditions. The average distilled-water contact angle was 21 ± 4°. The slip angles under oil-wet, water-wet and dry conditions were improved by the laser surface treatment compared with the bare SLS glass, and the associated slip risk was clearly diminished. The toughness of the annealed SLS glass was susceptible to a laser energy density above 0.23 J/mm^2, whereas the heat-strengthened SLS glass well tolerated the laser surface treatment within the investigated range of energy densities. A bending strength analysis in comparison with the bare SLS glass revealed 67% and 74% preservation of the Weibull characteristic bending strength for the annealed and heat-strengthened SLS glass, respectively. When such a decrease was combined with the observed increment of the Weibull modulus, the result was the preservation of the minimum expected bending strength (failure probability of 5% and confidence interval of 95%) for the tested configuration. The obtained results for the surface roughening and mechanical strength pave the way for the use of laser surface-modified plates in laminated glass elements that require slip resistant surfaces, with optimized strength calculation and weight reduction.

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Figure captions

Figure 1. Surface appearance of 25 mm width laser-modified bands on SLS glass and SEM micrographs of the processed surface: (**a**,**c**) CW laser processing (scanning speed 350 mm/min; laser energy density 0.23 J/mm^2); (**b**,**d**) pulsed-mode laser processing (scanning speed 350 mm/min; pulse duration 70 μs; pulse repetition rate 3000 Hz; average laser energy density 0.23 J/mm^2).

Figure 2. Representative surface profiles acquired from the CW laser-processed surfaces with increasing scanning speeds (profile direction normal to the scanning direction).

Figure 3. Surface roughness of the laser modified surfaces with respect to the scanning speed, and measured in the directions perpendicular and parallel to the scanning direction: (**a**) arithmetic average roughness Ra; (**b**) average roughness depth Rz.

Figure 4. Average slip angle of the SLS glass modified surface in oil wet, water wet, and dry conditions, with respect to the laser energy density. The solid lines represent the average inclination values of the reference as-received SLS glass surface (note the logarithmic scale of the energy density axis).

Figure 5. Vickers microhardness indentations and radial cracks on the SLS glass surface: (**a**) annealed glass (CW laser processing, scanning speed 300 mm/min; laser energy density 0.27 J/mm^2); (**b**) heat strengthened glass, (CW laser processing, scanning speed 300 mm/min; laser energy density 0.27 J/mm^2).

Figure 6. Fracture toughness in the proximity of the laser modified surface with respect to the laser energy density for annealed and heat strengthened SLS glass. The solid lines indicate the average K_{Ic} values of the reference annealed and heat-strengthened SLS glass (laser energy density logarithmic scale; K_{Ic} obtained from the well-developed indentation radial cracks using the method established by Anstis [29]).

Figure 7. Lateral and perspective views of the distilled water contact angle: (**a, b**) as received glass surface; (**c, d**) after CW laser processing (scanning speed 350 mm/min; laser energy density 0.23 J/mm^2).

Figure 8. ATR IR spectra obtained from the as-received and laser-processed glass surfaces (scanning speed 350 mm/min; laser energy density 0.23 J/mm^2). Bands: Si-O-Si bending mode 758 cm^{-1}; Si-O-NBO stretching mode 890 cm^{-1}; Si-O-Si stretching mode 1020 cm^{-1} (shoulder).

Figure 9. Bending strength test: Weibull plot and cumulative failure probability plot for (**a, b**) reference annealed glass (Weibull characteristic strength σ_0 = 135 MPa; Weibull modulus m_{cor} =4,9); (**c, d**) laser surface modified annealed glass (Weibull characteristic strength σ_0 = 91 MPa; Weibull modulus m_{cor} =9,5). Note the different values in the horizontal axes of the Weibull plots.

Figure 10. Bending strength test: Weibull plot and cumulative failure probability plot for (a, b) reference heat strengthened glass (Weibull characteristic strength σ_0 = 165 MPa; Weibull modulus m_{cor} = 5,5); (c, d) laser surface modified heat strengthened glass (Weibull characteristic strength σ_0 = 122 MPa; Weibull modulus m_{cor} = 10,0). Note the different values in the horizontal axes of the Weibull plots.

Tables

Table 1. Hardness, fracture toughness, and fracture surface energy of the laser surface-modified glass samples and the reference glass (annealed SLS glass).

Scanning speed (mm/min)	Laser energy density (J/mm^2)	Hardness (HV0.5)	K_{Ic} (MPa·m$^{1/2}$) *Miyoshi* [30]	K_{Ic} (MPa·m$^{1/2}$) *Anstis* [29]	Fracture surface energy (J/m^2)
50	1.64	546±10	0.57±0.05	0.51±0.05	0.98±0.19
100	0.82	564±14	0.67±0.04	0.60±0.03	1.35±0.11
200	0.41	544±16	0.64±0.06	0.58±0.05	1.27±0.19
250	0.33	544±20	0.64±0.04	0.57±0.03	1.24±0.11
300	0.27	548±21	0.62±0.08	0.55±0.07	1.19±0.26
350	0.23	545±10	0.81±0.01	0.73±0.01	2.15±0.04
400	0.21	543±12	0.80±0.09	0.71±0.08	1.93±0.30
500	0.16	547±17	0.72±0.04	0.63±0.03	1.15±0.11
600	0.14	556±16	0.81±0.11	0.72±0.09	2.01±0.34
unprocessed glass reference values	-	554±13	0.81±0.06	0.72±0.05	1.96±0.19

Table 2. Hardness, fracture toughness, and fracture surface energy of the laser surface-modified glass samples and the reference glass (heat-strengthened SLS glass).

Scanning speed (mm/min)	Laser energy density (J/mm^2)	Hardness (HV0.5)	K_{Ic} (MPa·m$^{1/2}$) *Miyoshi* [30]	K_{Ic} (MPa·m$^{1/2}$) *Anstis* [29]	Fracture surface energy (J/m^2)
50	1.64	534±5	1.29±0.08	1.15±0.07	4.99±0.63
100	0.82	549±10	1.29±0.04	1.15±0.04	4.98±0.35
200	0.41	544±13	1.31±0.11	1.17±0.10	5.16±0.88
250	0.33	541±10	1.14±0.10	1.02±0.09	3.92±0.86
300	0.27	536±6	1.19±0.12	1.06±0.11	4.22±0.91
350	0.23	542±10	1.29±0.09	1.16±0.08	5.02±0.67
400	0.21	544±7	1.21±0.05	1.09±0.04	4.43±0.37
500	0.16	550±14	1.28±0.07	1.15±0.06	4.95±0.59
600	0.14	550±7	1.26±0.08	1.13±0.07	4.78±0.62
unprocessed glass reference values	-	541±9	1.28±0.06	1.16±0.05	5.07±0.47