LASER TREATMENT OF HIGH-PERFORMANCE KYNOL FIBERS – AN EXAMPLE AS ALTERNATIVE TOOL FOR COLORATION AND IMAGING ON SURFACES OF HIGH-PERFORMANCE FIBERS

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Abstract: *Novolac resins are used to prepare high-performance flame-retardant fibers, which are also supplied under the brand name Kynol fibers. In the current study, Kynol fiber materials are treated with a laser beam to introduce dark coloration at distinct areas on the textile surface. By this, imaging and writing on the textile surface is possible. For investigation, two different types of Kynol fiber materials are used – a non-woven fiber felt and a woven fabric. It is shown that a laser treatment of medium intensity can introduce a change to dark coloration with good rubbing fastness. The writing of letters and symbols onto fabrics is possible. However, treatments with strong laser intensity lead to significant fiber damages and low rubbing fastness. Nevertheless, the presented method is a promising tool to apply images onto flame retardant fabrics from high performance fibers, which are difficult to dye using conventional techniques of dyeing and printing.*

Key words: Novolac resin, Kynol fibers, laser finishing, CO2-Laser, coloration.

LASERSKI TRETMAN KYNOL VLAKANA VISOKIH PERFORMANSI – PRIMER ALTERNATIVNOG ALATA ZA BOJENJE I OSLIKAVANJE NA POVRŠINAMA VLAKANA VISOKIH PERFORMANS

Apstrakt: *Novolac smole se koriste za pripremanje vlakna za usporavanje plamena visokih performansi, koja se takođe isporučuju pod robnom markom Kynol vlakna. U okviru ovog istraživanja, Kynol vlakna su tretirana laserskim zracima kako bi se unela tamna boja na određene delove tekstilne površine. Time je omogućeno ispisivanje i oslikavanje na tekstilnoj površini. U istraživanju su primenjena dva tipa materijala sa Kynol vlaknima – filc od netkanih vlakana i tkani materijal. Nalazi se da laserski tretman srednjeg intenziteta može dovesti do promene u tamnu boju sa dobrom otpornošću na trljanje. Ispisivanje slova i simbola na tkanini je moguće. Međutim, tretmani sa jakim laserskim intenzitetom dovode do značajnih oštećenja vlakana i niske otpornosti na trljanje. Ipak, predstavljeni metod predstavlja obećavajući alat za nanošenje slika na tkanine od vlakana za uspoavanje plamena visokih performansi, koja je teško bojiti konvencionalnim tehnikama bojenja i štampe.*

Ključne reči: Novolac smola, Kynol vlakna, laserska završna obrada, CO2-Laser, bojenje.

1. INTRODUCTION

High performance fibers are fibers containing at least one outstanding property, which conventional fibers do not have. These outstanding properties can be e.g. high strength, high chemical stability, high thermal stability or flame-retardant properties [1]. One very prominent example for a flame-retardant high-performance fiber is Kevlar made from para-aramid. However, also flame-retardant fibers based on other polymer materials are developed [1, 2]. One innovative approach to realize flame retardant fibers is the use of polymer resins as fiber forming materials. Mainly two types of such resin fibers are developed and commercialized, these are melamin based resins and novolac resins [2, 3]. Fibers based on novolac resins are offered under the brand name Kynol fibers [3]. Kynol fibers are used e.g. for preparation of sealing materials and in heat shielding applications [3, 4]. The chemical structure of novolac resin fibers is presented in Figure 1. Novolac fibers contain originally a strong orange coloration, which is related to a low reflection of UV light and blue light (Figure 2).

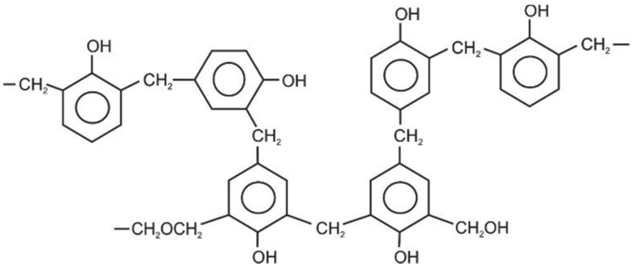

Figure 1: Chemical structure of novolac resin building up the Kynol fibers

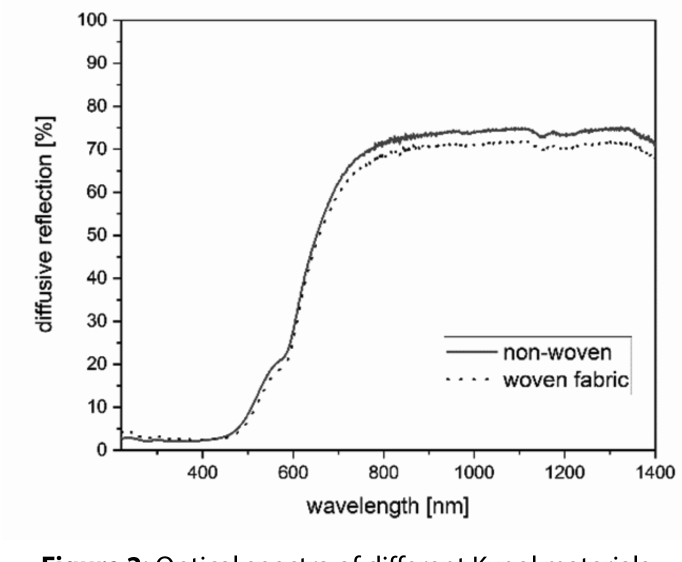

Figure 2: Optical spectra of different Kynol materials recorded in arrangement of diffusive reflection.

There are only few patents describing dyeing processes for Kynol fibers. However, similar to other high-performance fibers also Kynol fibers are difficult to dye with conventional dyeing processes. With this background, the aim of the actual study is the application of a laser to introduce dark coloration to Kynol fiber materials and enable by this coloration, imaging and writing on the fiber material. Nowadays laser finishing is an innovative method established in textile industry especially developed for the treatment of denim. One big advantage of laser finishing is the lower consumption of chemicals and a less waste water production [5, 6]. In this actually presented study, as Kynol fiber materials a non-woven fiber felt and a woven fabric are used. Beside measurements of the color properties, structural investigations are performed by scanning electron microscopy SEM and electron dispersive spectroscopy EDS.

2. EXPERIMENTAL SECTION

2.1. Materials

Two types of novolac resins fiber materials are used for investigations – a non-woven fiber felt and a woven fabric. These materials are supported by the company Kynol Europa GmbH (Hamburg, Germany). Both materials contain a significant orange coloration. The weight per area is 209 g/m^2 for the non-woven material and 297 g/m^2 for the woven fabric.

2.2. Preparation

The treatment of textile materials is done by a commercially available CO_2-laser, which is supplied by the company Trotec Laser Deutschland GmbH (Ismaning, Germany). The movement of the laser can be adjusted with a maximum speed of 3.55 m/s. For current preparations, a speed of laser in the range of 0.36 to 2.84 m/s is used. The speed of the laser determines, how long the laser is place on the same area of the textile surface. With a slower speed, the laser keeps longer on the same area and by this the amount of energy transfer to this specific textile area is stronger.

2.3. Analytical methods

The optical spectra of the fiber materials are determined by measuring the diffusive reflection by using a photospectrometer UV-2600 (Shimadzu, Japan), which is equipped with an integrated sphere. This measurement is done in the spectral range from UV light with 220 nm to near infrared light with 1400 nm.

The color properties of the samples are documented by using CIE *L*a*b** indices. These indices are determined by a device DATA Color 400 (Rotkreuz, Switzerland). The surface topography of investigated materials is recorded by scanning electron microscopy SEM by using a Tabletop microscope TM 4000 Plus supplied by Hitachi. This electron microscope is equipped with an EDS unit Quantax 70 supplied by Brucker. The EDS unit (electron dispersive spectroscopy) allows the quantitative detection of chemical elements on the surface of investigated materials. The dry rubbing stability of fabric coloration is determined using a crockmeter according to the standard DIN EN ISO 105-X12. Graded is the crock fastness by using a grey scale according to the standard DIN EN 20105-A02.

3. RESULTS AND DISCUSSION

3.1. Structural investigations

Novolac resins contain of the three chemical elements carbon, oxygen and hydrogen (Figure 1). The concentration of carbon and oxygen on the surface of the Kynol materials is determined by EDS. However, the chemical element hydrogen cannot be detected by this EDS method [7]. The EDS spectra of an untreated Kynol material and a laser treated Kynol material are compared in Figure 3. The spectroscopic peaks related to carbon and oxygen are clearly seen. For untreated Kynol fiber materials the weight ratio of carbon to oxygen is 77 to 23 on the material surface.

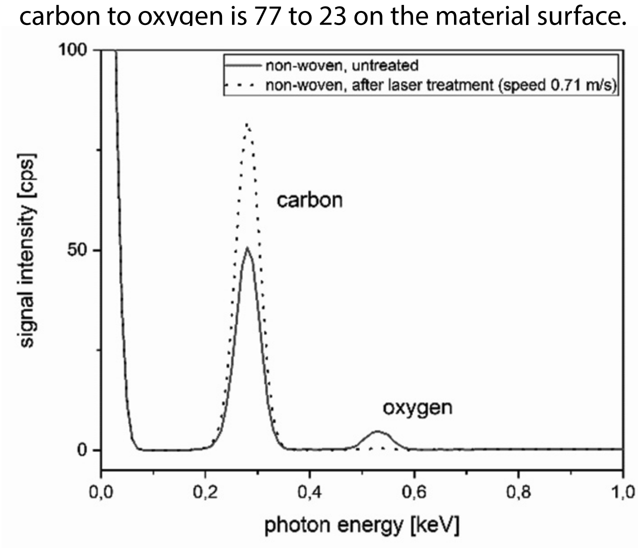

Figure 3: EDS-spectra of a non-woven made of Kynol fibers before and after laser treatment. The signals related to the chemical elements carbon and oxygen are indicated.

After laser application, the amount of carbon on the surface of the fiber material increases while the amount of oxygen decreases (Figure 3 and 4). The impact of the laser energy leads therefore to a kind of carbonization of the Kynol fiber surface. The amount of energy applied by the laser onto the fiber is determined by the speed of the laser driven over the fabric surface. With lower speed of the laser, the laser stays longer on the same fabric area, so higher amounts of energy are applied on the fabric area in case of slower laser speed. For this, a clear correlation of the chemical surface composition of Kynol fibers and the intensity of laser treatment is determined (Figure 4). With lowest speed of the laser (highest energy impact), nearly the complete oxygen is removed from the fabric surface and a nearly full carbonized fabric surface remains. For this case of intensive laser treatment on the non-woven material, the weight ratio of carbon to oxygen is 97 to 3.

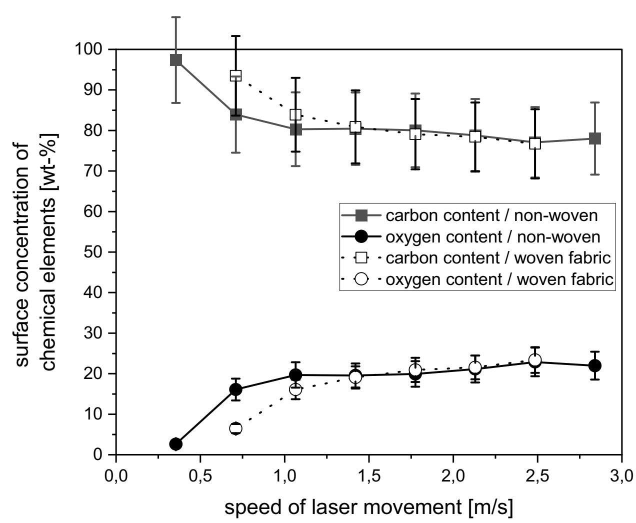

Figure 4: Surface concentration of chemical elements of Kynol fiber materials with different laser treatments. The concentration is shown as function of speed of the moving laser. The untreated Kynol materials contain 77 wt-% carbon and 23 wt-% oxygen on their surface. The surface concentration is determined by EDS-spectroscopy, which cannot detect the chemical element hydrogen.

The surface concentration after laser treatment determined for both investigated materials – non-woven felt and woven fabric – are for higher speed of laser movement nearly similar. Only, if the laser speed is decreased to values below 1.2 m/s a difference is visible. In case of lower speed, a higher content of carbon can be determined on the surface of the Kynol woven fabric compared to the non-woven felt. Probable the woven-fabric is more sensitive to

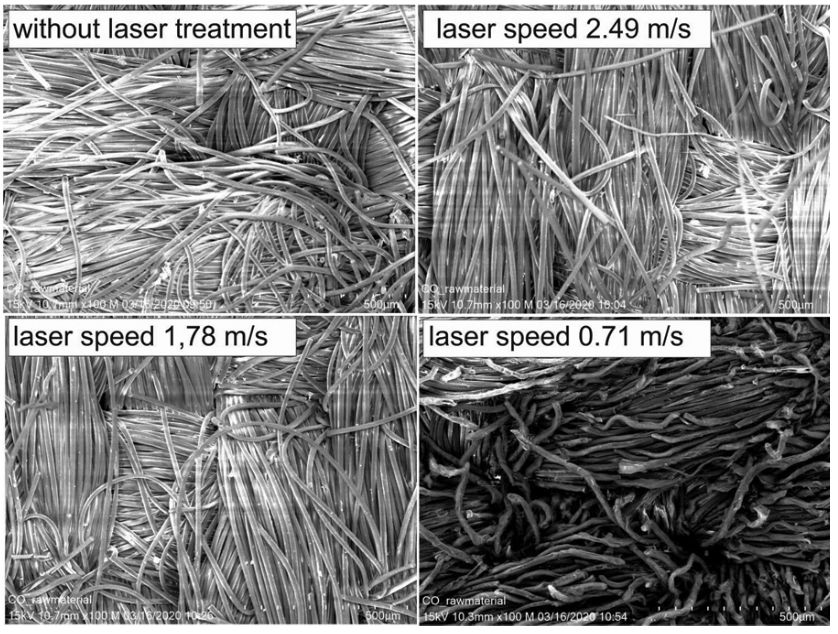

Figure 5: Microscopic images of Kynol woven fabrics before and after laser treatment. The images are taken by scanning electron microscopic SEM.

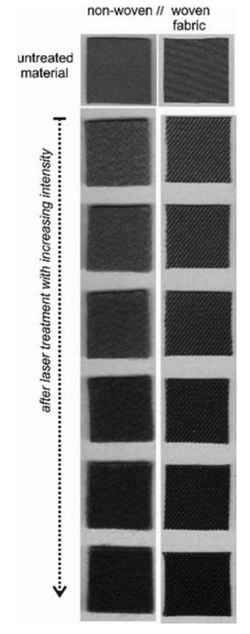

Figure 6: Samples of Kynol fiber materials (non-woven and woven fabrics) untreated and in comparison, after laser treatment with increasing intensity.

carbonization by the laser, because of a smooth fabric surface (Figure 4).

Microscopic images of woven fabrics from Kynol fibers are shown in Figure 5. Compared are a woven Kynol fabric without any laser treatment with three fabrics after laser treatment of different intensity. It is shown that a laser treatment of lower intensity does not lead to a visible fiber damage on this microscopic scale, even if by EDS a certain carbonization is determined. A laser treatment with strong intensity – introduced by lower speed of laser movement – leads to a significant damage of fiber and fabric structure. For this, it can be supposed that the mechanical stability of the treated fiber is not affected by slight laser treatment. However, laser treatment in strong intensity destructs the fiber significantly and by this the mechanical stability of fiber material is decreased.

3.2. Color properties

The color change to dark coloration is clearly indicated by visual observation (Figure 6). Both, the non-woven felt and the woven-fabric exhibit a continuous change from orange to black as function of increasing applied laser intensity. Beside the visual characterization, the change of color is also documented by CIE *L*a*b** indices (Figure 7). For the untreated Kynol fiber materials following indices are determined - woven fabric: *L**=47, *a**=23, *b**=46; non-woven fiber felt: *L**=48, *a**=22, *b**=49.

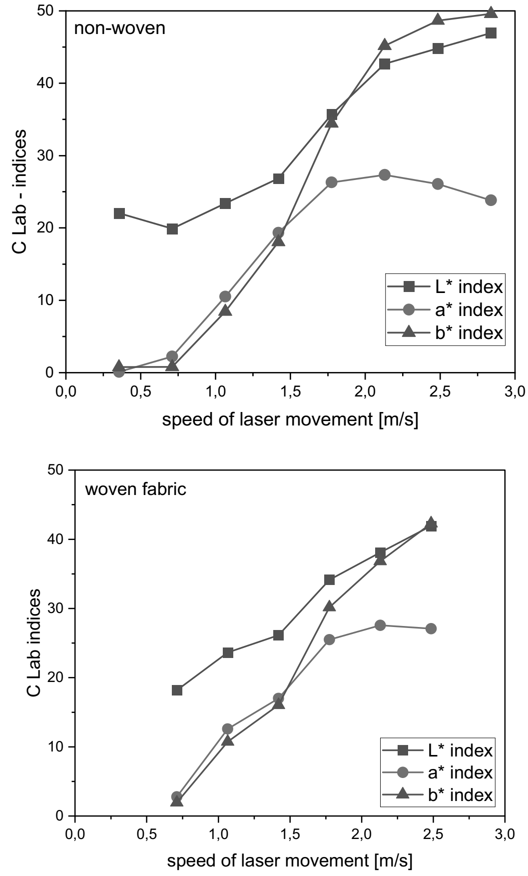

Figure 7: CIE *L*a*b** color indices of Kynol fiber materials with different laser treatments. The color indices are shown as function of speed of the moving laser.

The index *L** stands for the brightness of the textile sample. This value consequently decreases as function of stronger laser impact, so a darker coloration caused by the laser treatment is documented. The progress of carbonization determined by EDS measurements is here also reflected in the decrease of the *L** index. It is also seen for the non-woven material that for low laser speed from 0.7 m/s to 0.3 m/s no further decrease of the *L** index can be reached (Figure 7). This plateau value of around 20 for the *L** index is probable the limit of the finishing technique. The complete surface area is carbonized, so a further carbonization and by this a darker coloration is not possible.

For the untreated materials and for laser treatments with a speed of 1.8 m/s and higher, the index *a** shows values around 23. This number stands for a red content in coloration, which is obviously not changed if the laser impact is low or moderate. The sample gets darker but the red content is still the same. If the laser impact is increased, the index *a** is nearly linearly decreased to zero as function of decreasing laser speed (Figure 7). In that case, the laser burnt the coloration completely and a black textile surface remains. The decrease of the index *b** to nearly zero after laser application indicates a removement of the yellow colorant leading to a dark sample. The change in coloration at laser exposed areas can be used to create color changes at distinct areas of the textile surface. By this, a writing on Kynol woven fabrics is possible (see example in Figure 8).

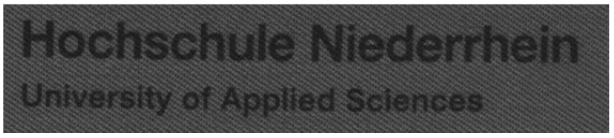

Figure 8: Examples for imaging and writing with laser finishing onto a woven fabric made of Kynol fibers.

The rubbing stability of the laser caused dark coloration is determined using a crockmeter (Figure 9). The resulting crock fastness according to standard DIN EN ISO 105-X12 is given in grades from 1 to 5, with grade 1 as lowest and grade 5 as strongest crock fastness. In comparison, the crock fastness of the non-woven material is slightly better compared to the one of the woven fabrics. For both materials a good crock fastness of grade 4 or higher is reached after low laser impact (laser speed higher 1.5 m/s). However, by this slight laser treatment only a moderate color change can be introduced. For stronger laser treatments, the crock fastness is consequently decreased, reaching lowest values for the strongest laser impact. It is clear, the laser treatment leads to a partly carbonization of the Kynol materials. This carbonization is responsible for darker color shades. However, due to damaging of the fiber by laser treatment, the carbonized areas exhibit only a limited stability against rubbing. For this, a strong laser indicated black coloration is naturally accompanied by a low rubbing resistance. Finally, there has to be a compromise made between intensity of color shade and the rubbing stability of this coloration.

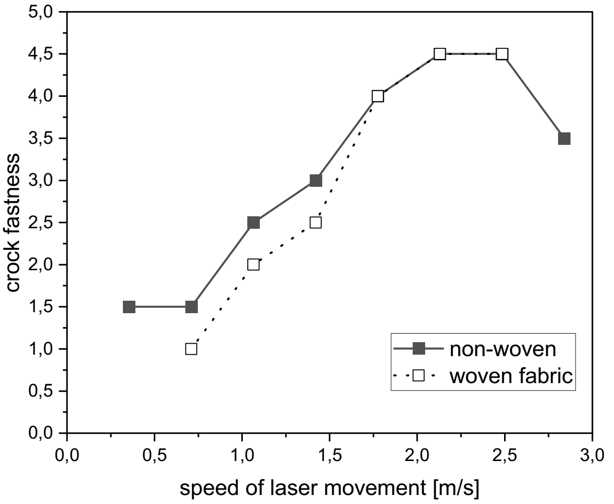

Figure 9: Crock fastness of the coloration of Kynol fiber materials with different laser treatments. The crock fastness is shown as function of speed of the moving laser. The crock fastness is determined using a crockmeter according to DIN EN ISO 105-X12.

4. CONCLUSIONS

Kynol fiber materials are investigated as an example for a flame-retardant high-performance fiber. Laser finishing of Kynol fiber materials is possible and can be used for coloration, imaging and writing on it. This laser finishing introduces a carbonization on the surface of the textile material and by this the color change to dark shade is introduced. However, laser treatment of strong intensity leads to fiber damaging accompanied by a low rubbing fastness. This is probable a certain limit of the laser finishing application. Nevertheless, the proof-of-concept is done on Kynol fiber materials and this application is probable also of high potential for other types of high-performance fibers.

Acknowledgments

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