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COMPOSITES THEORY AND PRACTICE

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PRELIMINARY EVALUATION OF PRODUCING POLYMER CLADDING ON GLASS FIBER DESIGNATED FOR FIBER LASERS

The paper presents a description of preliminary trials of covering glass-ceramic fibers with polymer resins intended for new fiber optics claddings. It occurred to be impossible to obtain a polymer film on the fibers without the effect of forming droplets using an epoxy resin with a relatively low viscosity (0.58 Pa·s). Reducing the thickness of the applied film by immersing the initially covered fiber ina solvent allowed the authors to obtain a uniform thin coat of 0.25 μm, which is too small for the practical application. Applying a gel-coat (high viscosity) as a covering liquid allowed a high thickness coating to be obtained. However, the thickness was very inhomogeneous - it varied from 2 to 30 μm. The most promising coating was gained with an acetone-based dispersion of ceramic powders with a viscosity of 0.8 Pa·s. It allowed the authors to obtain a coating thick enough to be technically applicable (> 10 mm), without the presence of droplets. This is an important guideline for further work on obtaining claddings for new optical fibers. The obtained results show the importance of viscosity and internal cohesion of the applied liquid for the effectiveness of its application to a solid base. Modifying the viscosity of liquids can in many cases be a technically simpler solution than improving wettability between the liquid and the given base.

Keywords: optical fibre, fibre laser, thin films, polymer resin, polymer cladding

WSTĘPNA OCENA MOŻLIWOŚCI UZYSKANIA PŁASZCZA POLIMEROWEGO NA WŁÓKNIE SZKLANYM PRZEZNACZONYM NA LASERY WŁÓKNOWE

Przedstawiono opis wstępnych prób nakładania powłok polimerowych na włókna szkło-ceramiczne, docelowo mających stanowić optymalne płaszcze na nowe światłowody dla laserów. Przy zastosowaniu żywicy epoksydowej o relatywnie niskiej lepkości nie udało się uzyskać filmu bez efektu formowania kropel. Zmniejszenie grubości nałożonego filmu poprzez zanurzenie włókna po pokryciu w rozpuszczalniku, pozwoliło uzyskać równomierną cienką warstwę o grubości 0.25 μm. Jest to grubość zbyt mała dla praktycznego stosowania tej metody. Zastosowanie na powłokę żelkotu (duża lepkość) pozwoliło uzyskać dużą grubość filmu, jednak jego grubość była bardzo nierównomierna na przekroju. Najbardziej obiecująca okazała się powłoka na bazie dyspersji acetonowej proszków ceramicznych o lepkości 0.8 Pa·s. Pozwoliła ona otrzymać film o grubości technicznie stosowalnej (> 10 mm) bez obecności kropli. Jest to ważna wskazówka do dalszych prac nad uzyskaniem optymalnego płaszcza na nowe włókna światłowodowe. Uzyskane wyniki uwidoczniły duże znaczenie lepkości i wewnętrznej spójności nakładanej cieczy dla skuteczności jej nałożenia na podłoże. Modyfikacja lepkości cieczy może być w wielu przypadkach rozwiązaniem technicznie prostszym niż poprawienie zwilżalności tą cieczą danego podłoża.

Słowa kluczowe: światłowody, laser włóknowy, cienkie filmy, żywica polimerowa, płaszcz światłowodu

INTRODUCTION

Fiber optics for lasers are specific types of fiber optics, used both in telecommunications (e.g. for amplifiers), as well as in other industries such as automotive, free space optics and medicine. They are characterized in particular by low damping, a simple construction and good luminescence properties resulting from doping with rare earth elements (REE) [1, 2]. It is advisable to look for new types of glass and ceramic materials suitable for pumping light in lasers, as there is a huge potential for the development of fiber-based lasers.

One of the basic problems associated with using optical fibers is to obtain a cladding on them (usually a multi-layer coating). Cladding acts as a shield against external effects, improves the fiber tensile strength and absorbs, reflects or selectively transmits light (pumping) - depending on the purpose of the fiber. Claddings on commercial glass fiber optics are obtained by applying an acrylic coating immediately after fabricating the fibers. This is not possible in the case of glass-ceramic fibers because they require reheating. For this type of fiber optics, coatings must be applied in a separate process. In addition, due to the process of devitrification of glass-ceramic fibers, the fabrication process requires a different approach [3].

The production of thin films on glass fibers is significantly different from coating elements with a greater geometry and flat surfaces. As a rule, the coating is applied from the liquid phase. The problem here is the tendency of the applied liquid to form droplets. It has been proven that after immersing the fiber in the liquid it will initially create a film of a certain thickness, which will then partially form droplets by local run-off. This is the result of the fiber-liquid-air system striving for equilibrium (with minimal free energy) and the driving force behind the changes are the forces resulting from the liquid's tendency to wet the fiber surface, the internal cohesion of the liquid and the force of gravity. This means that the equilibrium state of such a system is a fiber covered with a thin film of liquid sequentially passing into droplets (Fig. 1).

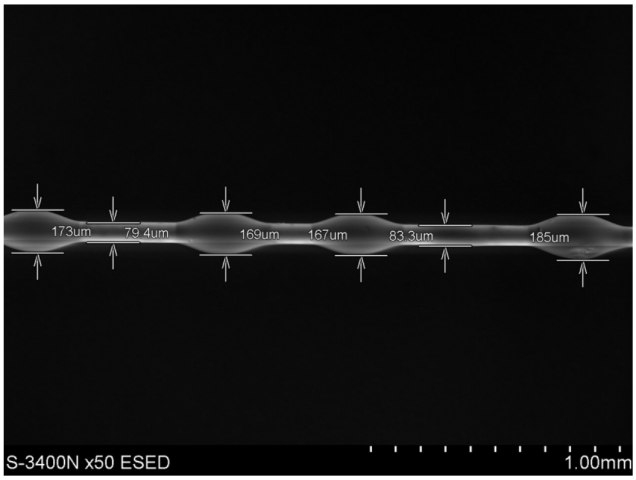

Fig. 1. Droplets of cured epoxy resin on glass fiber - scanning microscope image

Rys. 1. Krople utwardzonej żywicy epoksydowej na włóknie szklanym - obraz z mikroskopu skaningowego

Nonetheless, the process of the liquid flowing from the film into droplets only occurs when the film has a sufficiently large thickness. Study [4] shows the dependence of the nominal liquid film thickness on the glass fiber from the time after application. As the thickness of the film decreases, the size of the droplets decreases as well. Moreover, with a suitably thin film, droplets do not occur [4, 5]. This means that it is possible to obtain a film without droplets on the fiber, under the condition that $e \le e_c$, where: e - thickness of the applied film, e_c - critical thickness of the film. The initial film thickness on the fiber depends on many factors and is described by the following formula:

$$e_0 = 1.33 \cdot b \cdot Ca^{\frac{2}{3}} \qquad (1)$$

where: e_0 - initial film thickness [μm], b - fiber diameter [μm], Ca - capillary number (defined as $Ca = \eta \cdot V_0 \cdot \gamma^{-1}$, where: η - viscosity of the liquid [Pa·s], V_0 - coating rate [m/s], γ - surface tension [J·m^{-2}]).

It follows from the above discussion that in order to obtain a thin film on a fiber of a given diameter it is necessary to: use a low viscosity polymer, apply the lowest rate of dragging the fiber through the liquid polymer, ensure the highest possible surface tension between the fiber and the liquid (good wettability).

Meeting these conditions is often problematic, especially if the coated material is glass fiber that is poorly wetted by organic liquids. It is advisable to conduct a complex experimental analysis of the influence of the system: *the liquid-surface wettability - the viscosity of the liquid - the thickness of the applied film*, on the produced coatings.

The paper presents the results of preliminary technical research to obtain a curable resin cladding on a new photoconductive fiber intended for lasers. It is a novel glass-ceramic (oxygen-fluoride) fiber designed and produced by the authors on their own. An epoxy resin with appropriate mechanical and optical properties after curing was used as the main film-forming material. The main effect assumed and obtained in the presented testing stage is a set of guidelines for further experimental studies.

MATERIALS AND METHODS

The basis for the coatings are glass-ceramic oxygen-fluoride fibers with the chemical composition (% molar): $48SiO_2$-$11Al_2O_3$-$7Na_2O$-$10CaO$-$10PbO$-$13.2PbF_2$-$0.2ErF_3$-$0.6YbF_3$. The fibers were developed and produced as part of the authors' own work at the Faculty of Materials Engineering and Metallurgy of Silesian University of Technology. Epoxy resin LH288 with hardener H505 was used as the main coating material. The viscosity of this resin mixed with hardener was 0.58 Pas.

For cognitive experimental purposes (assessment of coatings obtained from viscous liquids), the HAVEL vinyl ester gel-coat catalyzed with METOX 50 peroxide was also used. For additional cognitive experimental purposes a non-thixotropic dispersion of a fine ceramic powder in an acetone base, as a medium viscosity liquid, was also used.

The diluent for the studied materials was dehydrated ethyl alcohol, only used if necessary.

Coating fibers with a liquid polymer was carried out on a specially assembled station (Fig. 2). The diameter of the capillary pipe was 0.75 mm.

The fiber was drawn through the reservoir containing resin. Next, the fiber was pulled through the capillary pipe (diameter d = 0.75 mm) to remove the local excess polymer and form a uniform coat. The fiber was then freely suspended at room temperature for 24 hours to cure the resin. After curing the resin, the coated fibers underwent evaluation. Evaluation of the obtained coatings was carried out using Hitachi S-3400 n and Phenom ProX scanning microscopes.

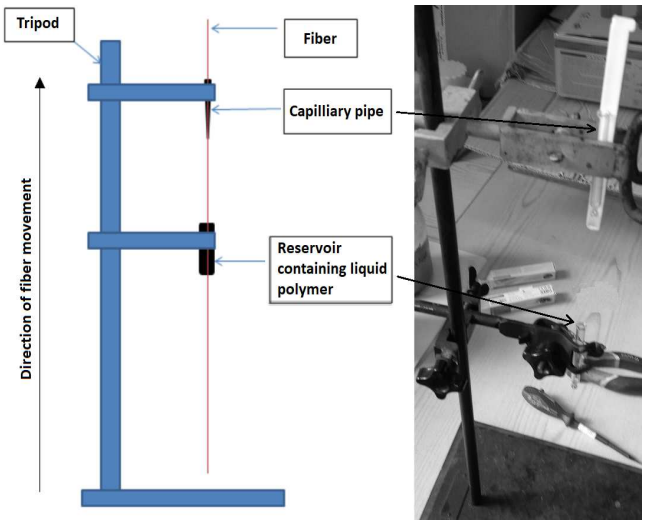

Fig. 2. Diagram of method fabricating polymer coating on fiber and photograph of stand

Rys. 2. Schemat metody nakładania powłoki polimerowej na włókno oraz zdjęcie stanowiska

EVALUATION OF RESULTS

The first group of tests to apply coatings by the method shown in Figure 2 were carried out using epoxy resin with a viscosity of 0.58 Pa·s. Immediately after applying the resin, droplets forming on the fiber were observed. After curing, the coating was subjected to microscopic evaluation. The side surface of the coated fiber as well as its cross-section was evaluated. A continuous coat as well as regularly spaced drops free from visible porosity were identified (Fig. 1). The lowest thickness of the obtained film outside the drop areas was about 1.3 μm (Fig. 3).

The greatest problem - anticipated before starting the research (see Introduction) - which eliminates the possibility of adopting the discussed solution in practice, is the formation of droplets on the coating and therefore instability (longitudinal) of the thickness of the obtained coat.

The second series of attempts to form coatings on the fiber was to produce a thinned layer of resin to minimize the local supply of liquid flowing to the forming droplets (see Formula (1)). For this purpose, an epoxy resin layer was applied to the fiber according to the procedure described above. Immediately after this, the excess resin applied to the fiber was removed by free immersion in acetone for 15 seconds. After removal, the fiber was suspended freely for 24 hours to cure the resin. No droplets appeared on the fiber, neither directly after immersion nor after curing the resin. The fiber cross-section was checked to identify the presence of the coating and its thickness. A thin film with a thickness of 0.25 μm was found (Fig. 4).

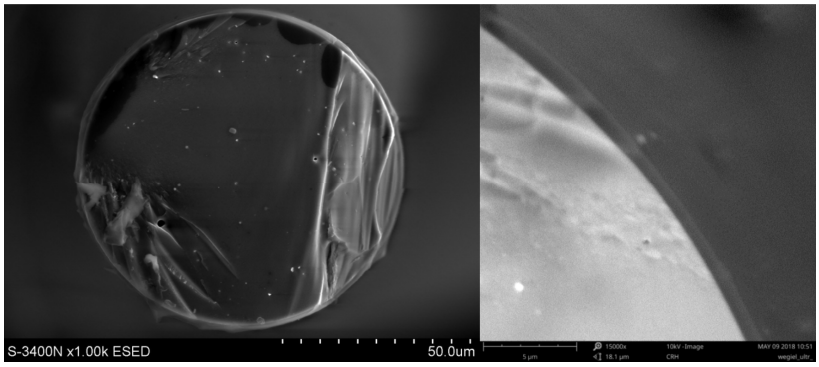

Fig. 3. Coating on fiber gained using epoxy resin, viscosity 0.58 Pa·s

Rys. 3. Powłoka na włóknie uzyskana z użyciem żywicy epoksydowej o lepkości 0.58 Pa·s

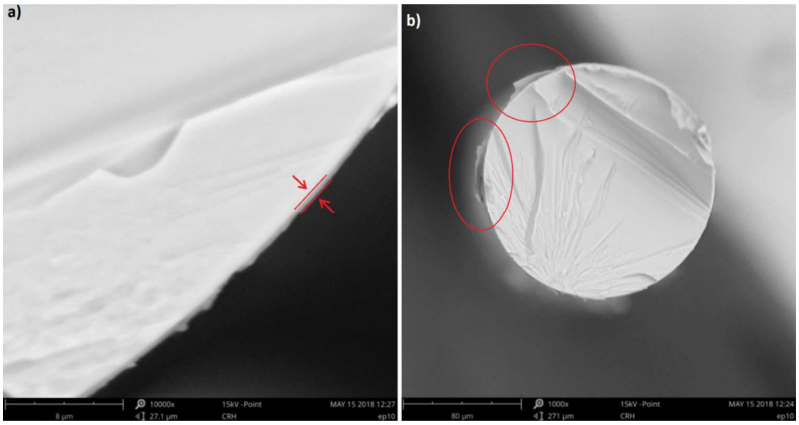

Fig. 4. Thickness of film on fiber after free immersion in acetone: a) visualization of obtained coating thickness, b) visualization of detachment and wrapping of coating caused by work of knife during fiber cutting

Rys. 4. Grubość filmu na włóknie po swobodnej immersji w acetonie: a) wizualizacja grubości uzyskanej powłoki, b) wizualizacja oderwania i zawinięcia powłoki spowodowanego pracą noża podczas cięcia włókna

The lack of droplet formation is a positive effect, however, the obtained coating is evidently too thin to be of practical use.

In order to use the previously described method to gain a thicker coat, a vinyl ester gel-coat was used. It should be emphasized that the gel-coat was used as an available liquid of a suitable viscosity, only for cognitive purposes and it is not planned to be used in practice as a component in optical fiber technology. After dragging the fiber through the gel coat, the drop effect (see Fig. 1) was not found. The surface and cross-section of the coating after curing were examined using a scanning microscope (Fig. 5).

The surface seems smooth. Nevertheless, the cross-section shows that the created coat is not uniform (in the thickest place it is approx. 30 μm, and in the thinnest approx. 2 μm). Moreover, when cutting the fibers, the sheath intensely detached from the fiber, probably more due to the high thickness, causing intense cross-sectional interaction with the cutting tool, than due to the particularly weak connection at the interface between the glass and the gel-coat.

The last experiment in this preliminary study was to carry out the procedure of producing a coating (according to the scheme described above) using liquid with the assumed optimal viscosity and a good wettability to glass. As such a liquid, a dispersion of ceramic powders in an acetone base (acetone + acrylic emulsifier) with a viscosity of 0.80 Pa·s was used. The results of microscopic observation of the obtained coating after curing are shown in Figure 6.

It was found that the surface quality of the coating is satisfactory and it shows no tendency to form droplets. A good connection between the coating and the fiber, and a homogeneous thickness of over 10 μm, was also found.

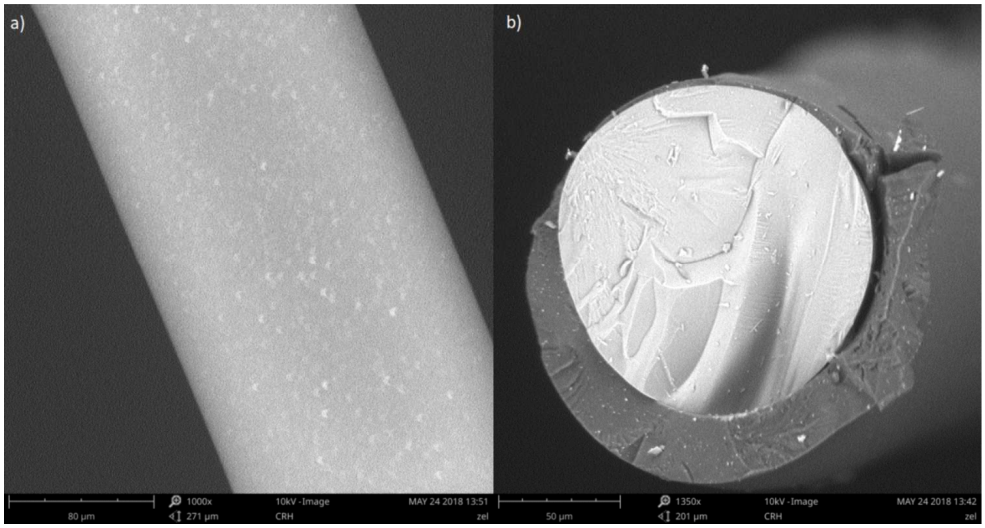

Fig. 5. Gel-coat coating on fiber - scanning microscope image: a) outer surface of coated fiber, b) cross-section of coated fiber

Rys. 5. Powłoka z żelkotu na włóknie - obraz z mikroskopu skaningowego: a) powierzchnia zewnętrzna pokrytego włókna, b) przekrój poprzeczny pokrytego włókna

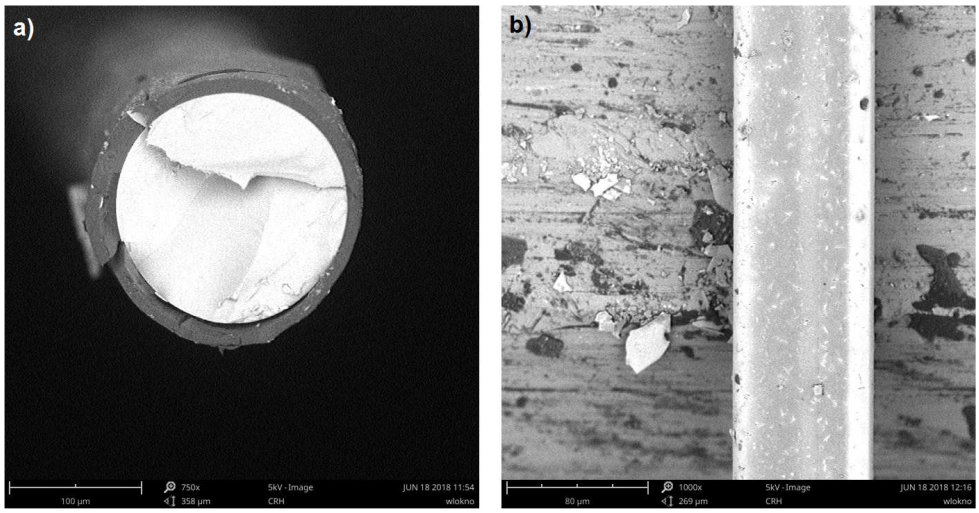

Fig. 6. Coating obtained from acetone dispersion: a) cross-section of fiber with coating - visible good connection of layer with fiber surface and uniform thickness exceeding 10 μm, b) image of fiber surface - good stability of applied coating quality and no drop formation

Fig. 6. Powłoka z dyspersji acetonowej: a) przekrój włókna z powłoką - widoczne dobre połączenie warstwy z powierzchnią włókna i równomierna grubość powyżej 10 μm, b) obraz powierzchni włókna - widać dobrą stabilność jakości nałożonej powłoki i brak tworzenia kropli

Based on the above observations and the practice of wetting glass fibers with liquids, it can be observed that the problem of covering fibers with liquid film-forming agents concerning their viscosity and particular level of wettability, can be described by four boundary models of fiber-liquid system behavior (Fig. 7).

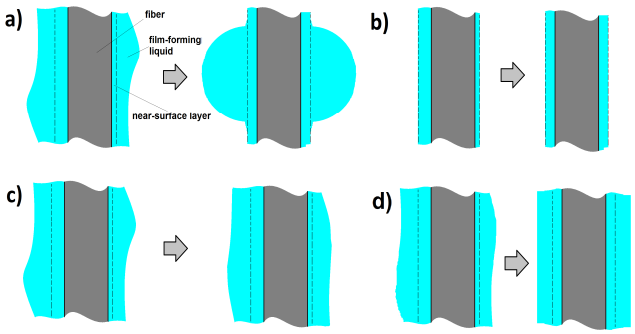

Fig. 7. Behavior models of film-forming liquid applied to fiber. Moment immediately after application of liquid and moment after stabilization of physico-chemical equilibrium is shown for each case: a) high film thickness and low viscosity (forming droplet), b) low film thickness and low viscosity (uniform, thin film without disturbances, no droplet formation), c) high film thickness and high viscosity (non-uniform, thick coating is created, no droplet formation), d) high film thickness and optimized viscosity (desirable option - uniform, thick coating without disturbances or droplet formation)

Rys. 7. Modele zachowania się cieczy powłokotwórczej naniesionej na włókno. Dla każdego przypadku pokazano wygląd fragmentu włókna tuż po swobodnym naniesieniu cieczy i po ustabilizowaniu się stanu równowagi fizykochemicznej: a) duża grubość filmu i mała lepkość (tworzy się kropla), b) mała grubość filmu i mała lepkość (tworzy się równomierna, cienka powłoka bez zaburzeń, brak tworzenia kropli), c) duża grubość filmu i duża lepkość (tworzy się nierównomierna gruba powłoka, brak tworzenia kropli), d) duża grubość filmu i zoptymalizowana lepkość (opcja pożądana - równomierna gruba powłoka bez zaburzeń i tworzenia kropli)

In the case of high film thickness and low viscosity liquid, and with poor wetting, gravitational force and the tendency of the *liquid-solid-gas* system to decrease the internal energy, cause droplet formation (Figs. 7a, 1 and 3). At a low thickness of the applied liquid film and - at the same time - its not very high viscosity (Figs. 7b and 4), there is a high probability of forming a uniform layer (low viscosity will allow free flow and stabilization of the equilibrium with a constant film thickness), without droplets, though, at a small thickness. If in turn we are dealing with a large film thickness and a high viscosity liquid (Figs. 7c and 5b), droplets will not form. However, the coating is not applicable in practice - it is thick but non-uniform. The high viscosity prevents the liquid from flowing freely and forming any shape other than that imparted during application. We assume that an optimum option exists for the system: *liquid-surface wettability - the liquid viscosity - thickness of applied film* (depending, among others, on the application rate), at which uniform film thickness, the lack of droplets and a sufficiently thick film occur (Figs. 7d and 6a). Initially proving the existence of such a system is the main achievement of this study.

SUMMARY

The paper presented the results of preliminary research on polymer coatings applied on glass-ceramic fibers intended for fiber optics. A discussion and proposal of models for the behaviour of the fiber-liquid-air system depending on the viscosity of the liquid and the thickness of the applied film were also presented. By using an epoxy resin with a relatively low viscosity, it was not possible to obtain a film without the effect of forming droplets. Reducing the thickness of the applied film by immersing the formerly coated fiber in solvent allowed the authors to obtain a uniform thin coat with a thickness of 0.25 μm, which is much too low a value according to the requirements. Applying a gel-coat (high viscosity) allowed a high thickness coating to be obtained, however, its thickness was not uniform. The most promising coating was gained from a dispersion of ceramic powders in acetone with an optimally chosen viscosity (0.8 Pa·s). It allowed us to obtain a technically applicable coating without creating droplets. Concerning this result, in further studies we will strive to form a coating with a similar viscosity, but with optimal optical properties.

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