Research Article
Application of Fluorescent Label in Polymer Nanofibers

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The electrospinning of fluorescent probe polyamide 6 doped by 7H-benzimidazo[2,1-a]benzo[de]isoquinolin-7-on is presented as a model processing photoluminescent nanofibers. The presence of the fluorescent probe in the fiber layers was confirmed by attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR); the surface nanofiber structure was described by high-resolution fluorescence microscope and scanning electron microscope images. The prepared nanofibers with the fluorescent label were further characterized by fluorescence spectroscopy, both in the solid phase and in the solution.

1. Introduction
The electrospinning technique is, principally, very simple and efficient method for producing polymer nanofibers from solutions or melts [1]. This technique has been known since the early 20th century. However, a significant progress in this area has been achieved during the past few years due to the wide range of nanofibers applications as novel materials in various devices and the producing of the synthetic polymer nanofibers on an industrial scale [2–5]. Polymer fiber could be applied, for example, as tissue scaffolds [6–9], filtration devices [10, 11], and fibrous reinforcements in synthetic and biological composite materials [12–14]. Nanomaterials might be used simultaneously in production of synthetic blood vessels, skin, or healing agents. Such materials could also be used as suitable matrices for the growth of stem cells. Moreover, during recent decades, the fluorescent conjugated polymers and their use as active components in organic light-emitting diodes, photoconductors, and sensors give the electrospinning technique farther attractiveness to be leader technology [15–17]. The electrospinning is applicable practically to every soluble or fusible polymer. Nevertheless, beside the most common polymer nanofibers, this technique has found an application in the preparation of metal, glass, ceramic, and carbon nanofibers [18, 19].

Using the electrospinning method, a different type of polymer can be fabricated as nanofibers. Their diameters, shapes, and configurations can be controlled using the adjustable parameters in the actual spinning process. At the same time, it is possible to apply a thin layer of selected polymers on virtually any surface.

Among large quantities of nanomaterials, polyamide-based nanocomposites are mostly applied in industry. This material has been used in connection with electrospun in many applications [20–23], for example, as part of the sensor [24]. PA6 has an ever wider application in nanomaterials [25–31]. The importance of such materials was capped by the first patent by Toyota on nylon 6 nanocomposite [32]. The main
problem is the difficulty of transferring the results from the laboratory to industrial processing [33, 34].

In this work, we have chosen 7H-benzimidazo[2,1-a]benzo[de]isoquinolin-7-one (NBI) for incorporation into PA 6 matrix by the electrospinning process. NBI is a very known fluorescent marker for labeling of various materials, and at least as a fluorescent color in reflective material [35]. The potential of labeled fibers is being, for example, as a component of composite materials (epoxy resins) or as safety agent in the industry.

2. Experiment

2.1. Materials and Instrumentation. NBI was prepared according to procedure described in the literature by the reaction of 1,2-benzenediamine and 1H,3H-naphththo[1,8-cd]pyran-1,3-dione [36] as shown in the reaction Scheme 1. The host matrix PA6 was purchased from BASF company. The concentration of polymer (PA6) in a solvent was 12 wt.%, the concentration of NBI in dissolved polymer was 10 wt.%, the electrode distance was 180 mm, the frequency of AC voltage applied was 50 Hz, and the current was 0.004 mA.

ATR-FTIR spectra were measured using Bruker Vertex 80V spectrometer. The solid samples were measured in attenuated total reflection mode using a diamond crystal. The sample was evacuated to 2.51 hPa. Spectral range was calibrated from 4000 to 600 cm−1. Each spectrum was scanned 100x. Bruker OPUS software was used for spectra evaluation and the baseline correction was done by “rubber-band.”

The images of the nanofibers were made by scanning electron microscope (SEM) Tescan MIRA3. Created nanolayer was fitted using sticky stick on the pad and its surface was covered by 30 nm gold layer. The samples were measured using secondary emission mode, depth regime with 15 kV, working distance (WD) of 10 mm, and 20,000x magnification. The contrast-enhancing coloring was used for contrast visualization. The fiber size was determined using software ImageJ software with manually located fibers [37, 38].

Fluorescence microscope was used to image the features of prepared sample. The images are in 5 Mpx resolution and acquired and processed using Levenhuk ToupVieW used UV source with a wavelength of 365 nm; the images were corrected on the light temperature of 5500 K (white light). The reflected light images are also corrected to white light (a temperature of light source, 4000 K). All photos are taken at identical exposure settings (58 ms).

2.2. The Preparation of the Solutions for the Formation of NBI Doped PA6 Nanofibers. The process of nanofibers production using electrospinning technique is influenced by many parameters, such as viscosity, temperature, polymer type, and solvent. The selection of the optimum solvent plays especially in the mixture of polymeric matrix (in our case PA6) and additive (NBI) a big role in the success of electrospinning process [32].

The polymeric matrix PA6 was dissolved in 10 ml trifluoroacetic acid (TFA) to create 12 wt.% concentration of viscous polymer solution. NBI was added to the PA6 solution in 10 wt.% of the total weight. The solvent as well as the concentration was chosen on the base of literature [32]. The whole mixture had been homogenized for 30 minutes in ultrasound apparatus before fiberizing.

Nanofibers were formed from the rod electrode using Elmarco Nanospider™ NSLAB 500 pilot plant unit (Figure 1). Using electrospinning technology, the nanofibers were obtained from the free surface of the polymer solution. Polypropylene (PP) foil was used as the supporting material covering the grounded electrode. The drops on the rod were formed in approximately the same size and each drop was fiberized for at least 8 minutes. Nanofibers were excised together with the supporting PP foil and allowed to dry for one hour at 25°C in order to evaporate the rest of the solvent. The values of fiberized polymer solutions and parameters of the electrostatic field are shown in Table 1.

3. Results and Discussion

The fluorescent probe was synthesized according to the reaction mentioned in Scheme 1.

The synthesized NBI was used as the additive into the PA6 matrix (NBIPA) and the nanofibers were created. Figure 2 shows the electron microscopy images of nanofibers composed of PA6 without NBI (left) and PA6 with NBI (right) in different magnifications.
Scheme 1: Synthesis of the fluorescent probe NBI.

From Figure 2, it is evident that the fibers created from the mixture of PA6 and NBI create unsmooth fibers with randomly arranged needles, easily observed in the snaps of fibers (right), whereas the fibers created from pure PA6 seem to be relatively homogenous, smooth without structure irregularities (left).

The needle structures are probably created as a result of presence of NBI. Simultaneously, the average width was determined from the SEM snaps, where 10 representative fibers were manually chosen, their borders were marked, and fiber width was determined (Table 2). Later, the presented

![Scheme 1: Synthesis of the fluorescent probe NBI.](image)

![Figure 2: SEM images of PA6 (left) and NBIPA (right) electrospun nanofibers in different magnifications.](image)

**Table 1: Parameters of the electrostatic field for PA6 and NBIPA.**

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<thead>
<tr>
<th></th>
<th>PA6</th>
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<th>NBIPA</th>
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<tbody>
<tr>
<td>Value</td>
<td>(d \text{ [\text{um}]})</td>
<td>Value</td>
<td>(d \text{ [\text{um}]})</td>
<td></td>
</tr>
<tr>
<td>Vol. count</td>
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<td>Vol. count</td>
<td>10</td>
<td></td>
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<td>Summation</td>
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<tr>
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<td>Min. value</td>
<td>0.70</td>
<td></td>
</tr>
<tr>
<td>Max. value</td>
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<td>Max. value</td>
<td>3.12</td>
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<tr>
<td>Mean value</td>
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<td>Mean value</td>
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<td></td>
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<tr>
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<td>Std. dev.</td>
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average fiber width was calculated as the average value of the measurement of 10 fibers. The average fiber width for fibers from pure PA6 was 250 nm, whereas the average fiber width for fibers containing PA6 and NBI was 2.02 μm. It means that the presence of NBI additive increases the average width of the fibers up to eight times.

The electrospun nanofibers prepared from pure PA6 and that prepared from its mixture with NBI were characterized by ATR-FTIR (Figure 3). The presence of NBI in created electrospun nanofibers is presented by the first two of four intense bands in the region between 1300 and 1700 cm\(^{-1}\) (the position of about 1350 and 1450 cm\(^{-1}\)). These bands are of low intensity for PA6. Furthermore, the presence of NBI in the electrospun NBIPA nanofibers is evident from the small dual-band around the region 900–1000 cm\(^{-1}\), which is absent for PA6.

We also investigated the fluorescence behaviour of NBI additive in the PA6 nanofibers. Figure 4 shows the snaps of nanofibers textile, where the fiber structure significantly shines in a comparison with the nanofibers textile without NBI additive. For comparison, PA6 without NBI can be observed in Figure 5 using a fluorescence microscope, so there is the evident difference between NBIPA and PA6.

The fluorescent spectra of both NBI in powder and NBIPA electrospun fibers are formed from a broad and structureless band. However, the fluorescence maximum of NBIPA is hypsochromically shifted by about 11 nm compared with the fluorescence maximum of NBI in solid phase (Figure 6). By comparison of the fluorescence intensity of NBI and NBIPA in solid phase, only insignificant difference was observed. Relative fluorescence intensities of NBI in solid phase are about ten times lower compared with the maximum intensity of NBIPA.
4. Conclusion

Electrospinning has been recognized as an efficient technique for the fabrication of polyamide 6 doping with NBI-fluorescent marker. Nanofibers with relatively regular structure, containing needle microstructures of NBI, were obtained. These modified fibers were studied using ATR-FTIR, SEM, fluorescence microscope, and spectrofluorimetric. It has been confirmed that the fibers exhibit the same fluorescence spectrum in comparison with NBI. The potential of the modified fibers is as a component of composite materials or as safety agent in the industry.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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