Thermal and Optical Properties of Polyimide Films with Dispersed SWCNTs for Laser Applications

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Single-walled carbon nanotubes (SWCNTs) demonstrate a high efficiency as optical elements for mode-locking in fiber lasers. A thin polymer film with dispersed nanotubes is a suitable approach to insert the element into the laser resonator. The main problem is that the polymer oxidative destruction temperature is much lower than that for SWCNTs. To form polymer–nanotube composites with a high threshold of thermal degradation, surviving under the relatively intense laser beams, a set of polyimides has been used. It has been shown that for the synthesized polyimides the temperature of degradation was in the range 500–530 °C, depending on the polymer. In the near-infrared range the polyimides were transparent, and the main absorption bands were detected at wavelengths less than 400 nm. A procedure of the fabrication of composite SWCNT/polyimide films was developed. The films were formed on transparent substrates, as quartz and glass slides.

1. Introduction

Single-walled carbon nanotubes (SWCNTs) are very promising saturable absorbers in near IR range due to the fast electronic relaxation from excited states.[1] For generation of femtosecond pulses in fiber lasers, the polymer films with embedded nanotubes are efficient to use.[2–7] However, one of the main obstacles is a low threshold of thermal destruction of polymer matrix, and, as a consequence, a low output power of laser used. SWCNTs may resist the oxidation up to 650 °C,[8] thought the smallest nanotubes may be oxidized at lower temperatures (350 °C).[8] In the polymer matrix, when the access of O_2 to the nanotubes is limited, this threshold may be even higher; in case of vacuum conditions thick nanotubes may be stable at more than 1700 °C.[9,10] To obtain the highest output power in mode-locking regime, it is desirable to use the relative stability of nanotubes, and to guarantee the thermal stability of the polymer matrix at least up to 500 °C. Polyimides are known as one of the most thermally stable polymers, so they have a big potential for solving this problem. For instance, for heterocyclic poly(pyridine-imide)s the thermal decomposition threshold was higher than 450 °C, and for some selected polyimides it was about 520 °C.[11] In work [12], it was shown that the modification of polyimides with multi-wall carbon nanotubes (up to 2 wt.%) led to the thermal stability increase, and the initial decomposition temperature upgrowth from 533 to 555 °C.

Polyimide matrix with dispersed SWCNTs may be effectively used for the mode-locking in fiber lasers.[13,14] The pulse durations of 314[13] and 391 fs[14] before the dispersion compensation have been achieved.

For optical applications, a uniform dispersion of nanotubes in the host polymer film is mandatory. The most substantial factor for obtaining individually dispersed NT is the molecular interaction between polyimide matrix and the nanotube walls.[15–21] In work [15], the impact of biphenyl groups on the NT separation was demonstrated. The high content of the aromatic rings in polyimide[16] also provided a good dispersion of nanotubes. Other possible ways to increase the nanotube separation were to use the carboxylated SWCNTs[17] or polyimides with grafted side-chains.[19]

Here, we focus on the dispersion of single-wall carbon nanotubes in various polyimides and optimization of formation of thermally resistive thin films with the uniformly dispersed nanotubes, which are prospective as optical elements for mode-locking and short-pulse generation in near IR range in fiber lasers.

2. Experimental Section

2.1. Materials

Commercially available (Sigma–Aldrich) CoMoCAT SWCNTs, with a mean diameter 0.7 nm, and HipCO SWCNTs with a broad distribution of the diameters 0.7–1.4 nm were used as the principal agents responsible for the saturable absorption.

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Polyimides used for fabrication of SWCNT composite film were synthesized at National Taiwan University of Science and Technology. The chemical sketches of all polymers are shown in **Figure 1**. Generally, n-methyl-2-pyrrolidone (NMP) from Sigma–Aldrich was used as a solvent.

The synthesis of some polyimides was reported earlier: TRELENA 003,[22] TRELENA 009-012.[23–25]

Synthesis of TRELENA 001, 002, 004–008 was performed in two steps. First, 2,2′-Bis(methyl)-4,4′-bis(trimellitimidophenyl) biphenyl (BMTB) was synthesized according to previous report.[26] Second, addition of various diamines allowed to synthesize various polyimides. A mixture of 0.90 mmol of diamine, 0.90 mmol of BMTB, 0.35 g of calcium chloride, 0.80 mL of triphenyl phosphite, 0.80 mL of pyridine, and 4 mL of NMP was refluxed for 3 h. The homogeneous solution was subsequently poured into a large quantity of methanol with constant stirring to precipitate polymer. The polymer was filtered and washed thoroughly with methanol and hot water, repeatedly, and dried at 120 °C under vacuum.

TRELENA 013 was prepared via polycondensation. To a stirred solution of 0.424 g (2 mmol) of *m*-tolidine in 5 mL of *N*-methyl-2-pyrrolidinone (NMP), 0.937 g (2 mmol) of *N*, *N′*-bis (1,2-cyclohexanedicarboxylic anhydride-4-yl) carbonyl-1,4-phenylenediamine (PPHT) was gradually added. Additional 15 mL of NMP was gradually added when PPHT reacted with *m*-tolidine. The mixture was stirred at ambient temperature for 6 h to form the poly(amic acid). Chemical imidization was carried out by addition of 2 mL of acetic anhydride and 1 mL of pyridine into the above-mentioned poly(amic acid) solution with stirring at 130 °C for 3 h. Then the polymer solution was poured into excess methanol. The precipitate was filtered, washed with methanol, and dried at 100 °C under vacuum to obtain TRELENA013 as white solid.

2.2. Optical Absorption Spectroscopy

Absorption spectra were registered with double-lined spectrophotometer Perkin Elmer Lambda 950. Spectral resolution was 1 nm. Suspensions were measured in 1 cm quartz cell. Films were fixed with the holder for thin samples.

2.3. Suspension Preparation and Film Fabrication

SWCNTs suspended in NMP with polyimides were sonicated by the ultrasonic tip Hielsher UP200 (power 200 W). Afterward suspensions were centrifuged in Beckman Coulter Optima Max-E in 8 mL tubes.

3. Thermal and Optical Properties of Polyimides

3.1. Optical Absorption of Polyimides in Suspensions and in Films

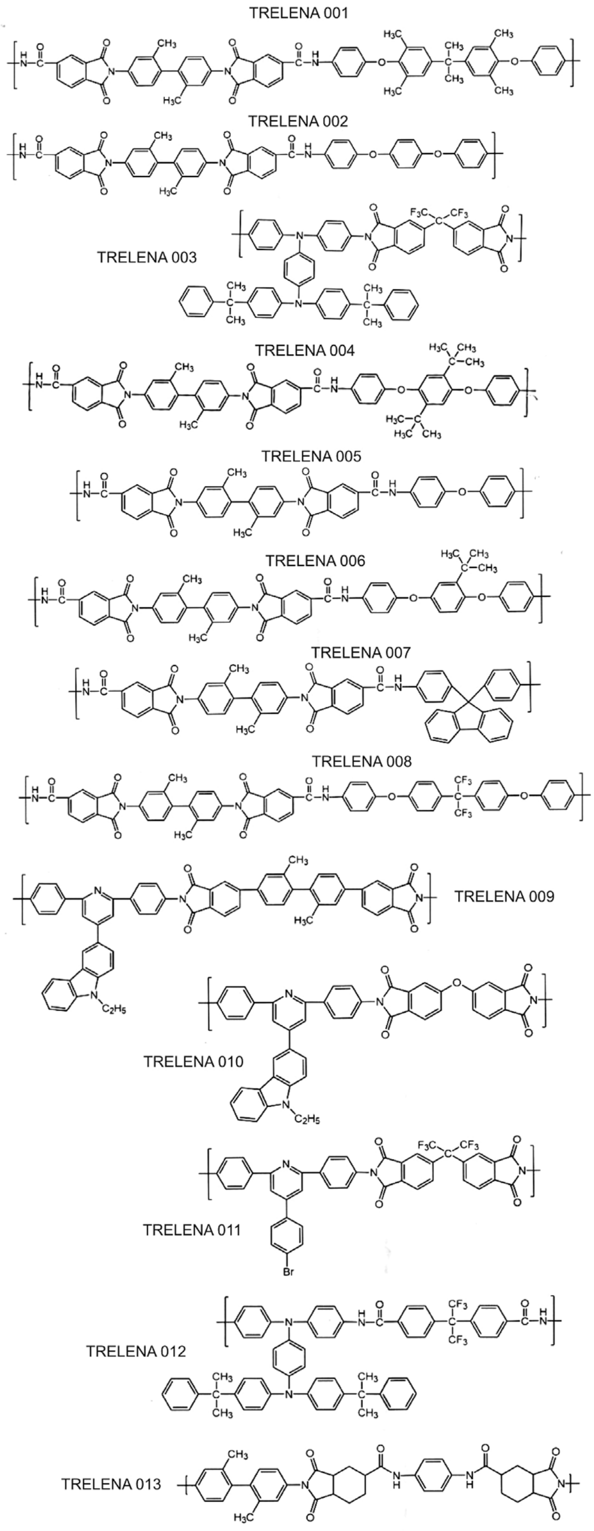

Figure 1. Chemical structures of polyimides TRELENA 001-013.

SWCNTs are very prospective saturable absorbers in IR range and can be efficiently used in fiber lasers as optical elements. The polymer matrix, in which nanotubes are embedded, should fulfill the following demands: the polymer should be transparent at the laser generation wavelength and thermo-stable in order to prevent the degradation of the film under the laser beam; it

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should also be able to disperse effectively and uniformly SWCNTs, in order to form the film with isolated individual nanotubes or with thin ropes of SWCNTs.

The optical absorption spectra were measured for the polymer solutions in various solvents (depending on the polyimide type, in NMP, chloroform, DMF, and others), and for the films on the glass substrates (the solvents were evaporated). The spectra of the selected polyimides are shown in **Figure 2**. The main absorption lines of all polyimides were in UV range (<400 nm).

In the range 1000–2000 nm, where Er^+, Tm, Yb fiber lasers emit the light, the highest transparency was demonstrated by polyimides TRELENA 009-011, 013. For these four polymers the measurements of thermal stability were performed. The polyimides with BMTB in the monomer base (TRELENA 001, 002, 004–008) were less transparent in general, and the absorption shoulder was shifted from UV toward visible range.

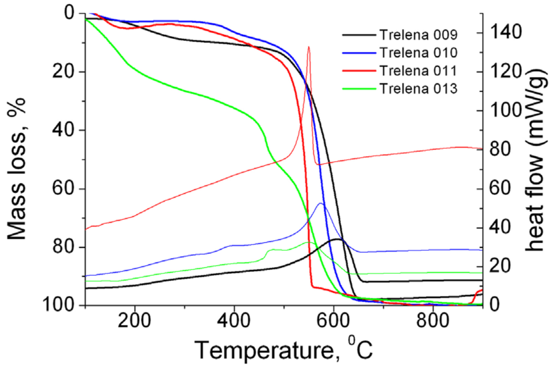

Figure 3. Mass loss and heat flow in temperature range 100–900 °C for polyimides TRELENA 009-011, 013.

3.2. Thermogravimetry (TG) and Differential Scanning Calorimetry (DSC) of Polyimides

Figure 3 shows thermogravimetric measurements, i.e., loss of mass and heat flow in the temperature range 100–900 °C for polyimides TRELENA 009-011, 013. It is seen, that below 250 °C the evaporation of solvent and residues of water takes place, as there is a slight mass loss. The main feature in graphs is observed at 500–530 °C, and it is caused by thermal oxidation of polyimide samples. From dependence of mass flow the threshold of the polymer decomposition was estimated by finding the temperature, corresponding to the maximum of the mass loss derivative. It was equal to 552 °C for TRELENA 009, to 535 °C for TRELENA 010, to 535 °C for TRELENA 011 and to 530 °C for TRELENA 013. From data of differential scanning calorimetry the very beginning of the thermal destruction of the polymer was also estimated, and it occurred at 500 °C for TRELENA 009, to 524 °C for TRELENA 010, to 524 °C for TRELENA 011, and to 510 °C for TRELENA 013.

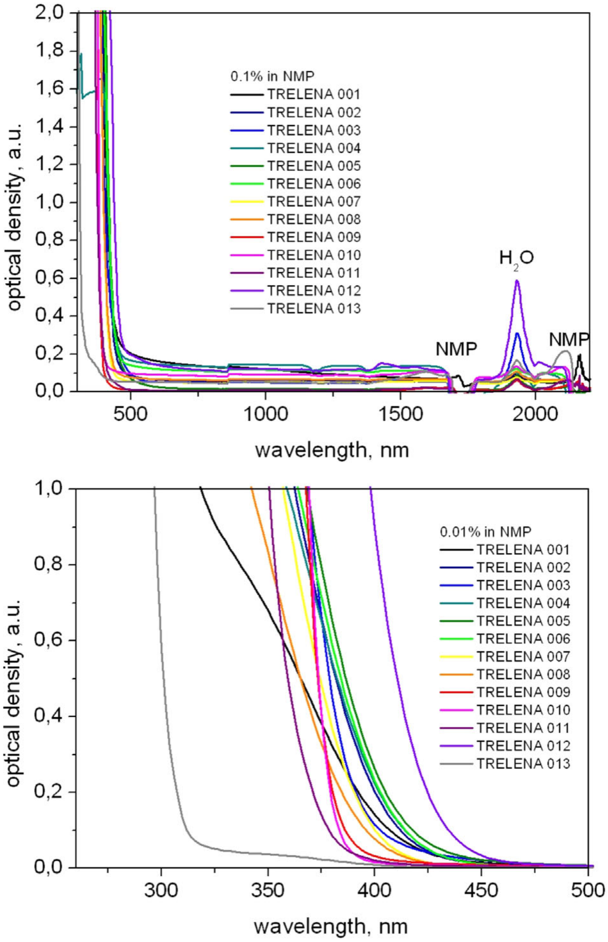

Figure 2. Optical absorption spectra of selected polyimides.

4. SWCNT/Polyimide Composites

4.1. Fabrication of SWCNT/Polyimide Composites

SWCNTs could be dispersed in NMP. However, the concentration of the nanotubes is limited to 20 mg L^{-1},[27,28] and nanotubes tend to aggregate. According to Ref. [29], ultrasonicated and vacuum-filtered SWCNT dispersions in NMP are not completely stable, even at as low concentrations as 10 mg L^{-1}.

The presence of the polymer allows to create matrix and to isolate nanotubes from each other in the volume of the polymer film.

The uniform suspensions of SWCNTs and polyimide in NMP (or another solvent) were prepared. First, polyimide (1–2 wt.%) was dispersed in solvent and placed on the magnetic stirrer at 70 °C for 3 h. Then, SWCNT (0.01–0.03 wt.%) were added. In order to disrupt the nanotube bundles, the suspension was ultrasonicated during 1 h. Then, the suspension has been centrifuged to remove the large agglomerates, thick bundles, and heavy impurities (metallic particles of catalyst). The centrifuge acceleration and time of the centrifuging both are very important parameters. It has been revealed, that the accelerations less than 5000×*g* and time less than 10 min do not provide separation of the bundles and impurities, and even in the upper part of the tube the aggregation of nanotubes is substantial. When the

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acceleration is more than 100 000×g, the polyimide starts to form the gradient medium and partly sediments. That leads to the nanotube aggregation (**Figure 4**). Also the large amount of nanotubes goes to the bottom of the centrifuge tube. The long time (more than 30 min) of centrifuging leads to the nanotube sedimentation. The optimal conditions for the centrifuging were 30 000×g during 15 min; that permitted to obtain a relatively high concentration of nanotubes without a large aggregation.

The supernatant, containing isolated single nanotubes, was deposited layer by layer on the substrate at elevated temperature (90–100 °C).

To avoid the aggregation of the nanotubes, the suspension was re-sonicated each time before applying a new layer. The final composite SWCNTs/polyimide films are presented in **Figure 5**. Its thickness, depending on the number of layers, was in the range 10–20 μm.

4.2. Thermal and Optical Properties of SWCNT/Polyimide Composites

It is possible to vary the optical density of the film, applying few layers of SWCNT/polyimide suspension on the substrate, or using various time and acceleration of the centrifuging. Following the procedure described in Section 4.1, films with all available polymers were made. In **Figure 6**, the optical absorption spectra of the SWCNT/TRELENA 013 films on substrate and the free-standing films are shown.

Here, the nanotubes of different diameters were used in order to cover different ranges of wavelength. Depending on the diameter and chirality, each nanotube has its own unique set of absorption lines.[30,31] In case if there are nanotubes of many different chiralities, the absorption lines are combined and form together bands E_{11}, E_{22}, etc. For instance, in Figure 6A, one can see the band E_{11}, where prevails the peak at 1020 nm. It originates from (7,5) nanotubes with diameter 0.7 nm.[31]

For example, Yb fiber lasers have generation at 1.06 μm, so the small nanotubes with diameter 0.7 nm are suitable, as their absorption band E_{11} lies at 1000–1100 nm. For Er lasers, generation of light has maximum at 1.55 μm, and nanotubes of larger diameters are needed. In Figure 6B, there is the optical absorption of nanotubes with diameter distribution 0.7–1.4 nm. One can see that there are well-resolved lines, corresponding to certain nanotubes, and the transition between the first van Hove singularities in the density of states is seen as band E_{11}, situated at 1000–1800 nm, with the most intense lines at 1200 and 1350 nm.

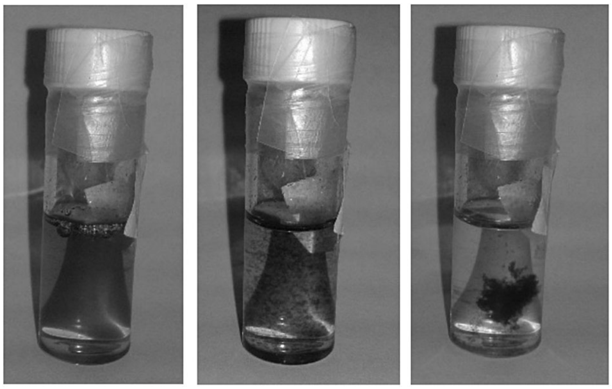

Figure 4. Aggregation of nanotubes in polyimide/NMP after the centrifuging at 150 000×g right after the centrifuging, after 20 min, and after 1 h.

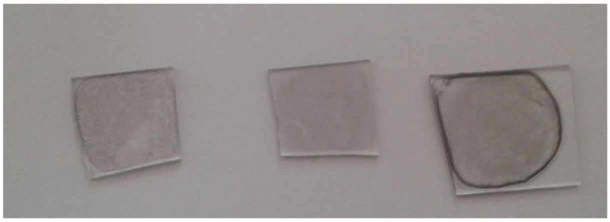

Figure 5. SWCNT composites with TRELENA 009, 010, 013 (from left to right).

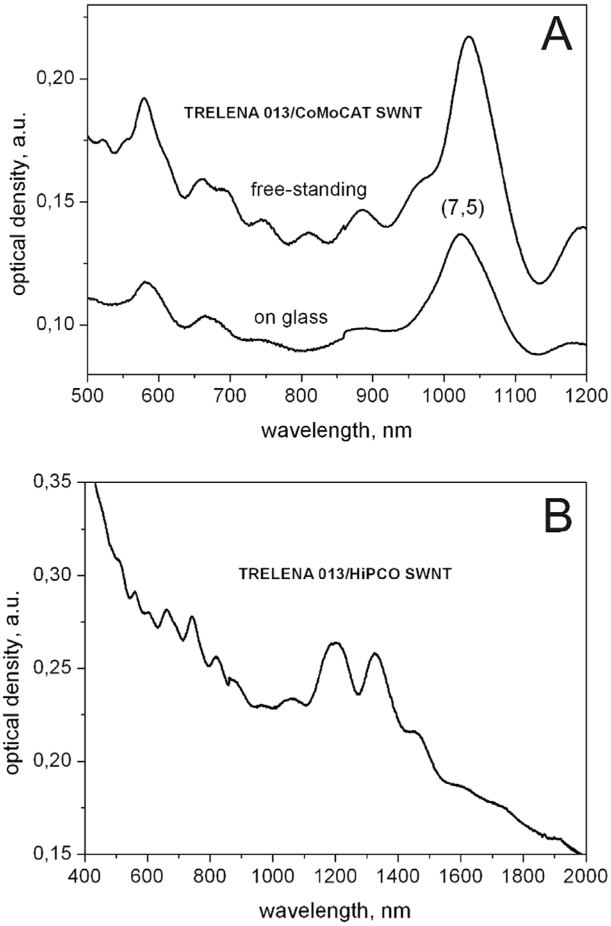

Figure 6. The optical absorption spectra of composite films SWCNT/TRELENA 013. A) Films with CoMoCAT nanotubes with small diameters (0.7 nm). B) Films with HipCO nanotubes (diameters 0.7–1.4 nm).

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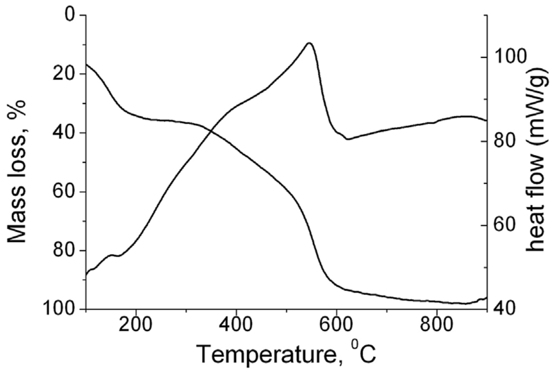

Figure 7. Mass loss and heat flow in the temperature range 100–900 °C for composite film SWCNT/TRELENA 013.

To estimate the influence of SWCNT presence on the composite thermal properties, the temperature-dependent measurements of mass loss and heat flow were performed on composite films SWCNT (CoMoCAT)/TRELENA 013 (**Figure 7**). The oxidation of the film took place at 527 °C, as it was estimated from the dependence of mass losses, and temperature threshold was estimated as 505 °C from DSC curve. These values are very close to those, obtained for the pure film of TRELENA 013 (containing no nanotubes). Probably, the content of nanotubes in polyimide film was too low to provoke the changes in thermal behavior of the composite.

5. Summary

The properties of 13 polyimides were compared with each other. Their optical properties, solubility in various solvents, and ability to disperse nanotubes were analyzed. The main absorption lines of all polyimides were in UV range (<400 nm). For the effective work of the saturable absorbers, it is necessary to minimize the absorption of the polymer matrix at the working wavelength of the laser. A few most acceptable samples were selected. They were transparent in the range 1000–2000 nm, where Er^+, Tm, Yb fiber lasers emit the light.

The temperature dependences of the mass losses (thermogravimetry) and of the heat flow (differential scanning calorimetry) were measured to estimate the thermal threshold of the polymer stability. For all the samples the thermal destruction starts at 500–540 °C.

The procedure of fabrication of composite SWCNTs/polyimide films was developed. The films were formed on the transparent substrate (quartz and glass). The optimization of the conditions of dispersion, centrifuging of the suspensions, and drying of the film has been performed. The final composite SWCNTs/polyimide films were uniform, and their absorption could be varied by changing the thickness of the composite film.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

composites, fiber lasers, polyimides, single-walled carbon nanotubes, thermogravimetric analysis

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