Nonlinear Absorbers Based on Multi-wall Carbon Nanotubes for Protection of Sensitive Elements of Electro-optical Systems and Vision Organs

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Abstract. The optical limiting of laser radiation in a wide range of wavelengths can be obtained using functionally substituted phthalocyanines adsorbed on the surface of multi-walled carbon nanotubes. Nonlinear optical material for this purpose can be produced in two ways: liquid dispersed medium and solid composites. This protection is a passive optical limiting substance when located in focus with a confocal system due to the manifestation of nonlinear optical properties during the passage of a sufficiently powerful laser radiation.

Keywords: Optical limiter · Composites · Carbon nanotubes (CNTs) · Phthalocyanines (Pc)

1 Introduction

To protect sensitive elements of electro-optical systems and organs of vision, active and passive optical systems are being developed, the main task of which is to limit the transmitted radiation to a safe level. Pulses of shorter duration than 30–50 ns can be attenuated using passive optical protection systems due to nonlinear optical limiting. Moreover, such a response speed is achieved only by some active means of optical protection [1, 2]. Widespread filters, based on linear attenuation of the light, equally attenuate both powerful and weak non-hazardous radiation, which makes it difficult to visually controlling technological processes, in particular, medical operations. In some cases, during the healing, direct observation of the area treated with the laser is required [3]. For these reasons, liquid dispersed medium (dispersions) and solid composites for

I. A. Parinov et al. (Eds.): *Physics and Mechanics of New Materials and Their Applications*, SPM 20, pp. 481–489, 2023. https://doi.org/10.1007/978-3-031-21572-8_41

optical limiting based on nonlinear optical effects are being developed. The main disadvantage of such nonlinear optical limiting is the lower degree of attenuation of laser radiation in comparison with active protective equipment based on liquid crystals. Therefore, the main purpose of such devices can be considered as the possibility of increasing the maximum allowable energy fluence, which the passive limiter is still able to limit within the allowable [4]. In case of damage by a sufficiently powerful laser radiation, “critical” organs such as eyes and skin can be affected [5]. It is possible to obtain a significant attenuation of laser radiation in a wide range of wavelengths using functionally substituted phthalocyanines (Pc) adsorbed on the surface of multi-walled carbon nanotubes (MWCNTs). With the same transmittance as liquid dispersions, the composites with pronounced nonlinear optical properties can be fabricated [6]. Also, film limiters are more suitable for practical use in means of protection against laser radiation. The main purpose of the obtained functional nanomaterials is the ability to attenuate high-intensity laser radiation without damaging the sensitive elements of electro-optical systems and organs of vision.

2 Experimental Part

Cyclotriphosphazene-substituted low-symmetry Pc ligand **1** [7] was adsorbed on the surface of MWCNTs (MWCNTs/Pc(**1**)) and used both in liquid dispersion and a solid state (see Fig. 1). To investigate optical properties of the samples, following methods were utilized: UV-Vis spectroscopy (Thermo Fisher Scientific™), Raman spectroscopy (LabRAM Horiba spectrometry complex with a HeNe laser, wavelength of 633 nm in the range of 100–4000 cm^{-1}), and nonlinear optical response using Nd:YAG Laser setup (532 nm wavelength, 16 ns pulses).

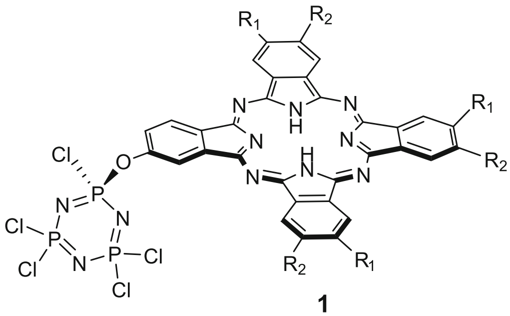

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Fig. 1 Chemical structure of cyclotriphosphazene-substituted monophthalocyanine (**1**)

2.1 Preparation of Liquid Dispersed Medium and Solid Composites

Liquid dispersions of MWCNTs/Pc(**1**) were prepared in dimethyl sulfoxide (DMSO), dimethylformamide (DMF) and distilled water. Sedimentation resistance was achieved

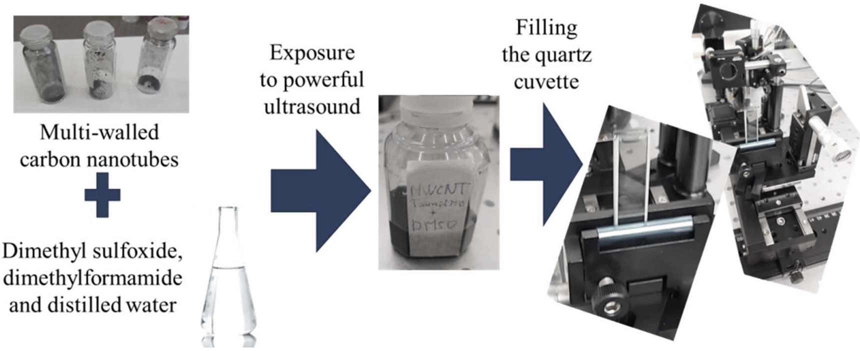

Fig. 2 Scheme for the preparation of the liquid dispersions of MWCNTs/Pc(**1**)

by ultrasonic treatment with a homogenizer Sonicator Q700 (Qsonica, Newtown, U.S.), used for 1 h at a power of 40 W in a small volume of liquid 50 ml (Fig. 2).

However, in practice it is convenient to use solid materials. The preparation of the corresponding composites was carried out by mixing dispersions with polymethyl methacrylate (PMMA) at 80 °C. A solid sample can be prepared using DMF and DMSO in which it is possible to dissolve PMMA at temperatures of the order of 80 °C (Fig. 3). Liquid dispersions MWCNTs/Pc(**1**) can be obtained with sedimentation resistance in distilled water, but homogeneous dispersions cannot be obtained with PMMA for further preparation of the composites.

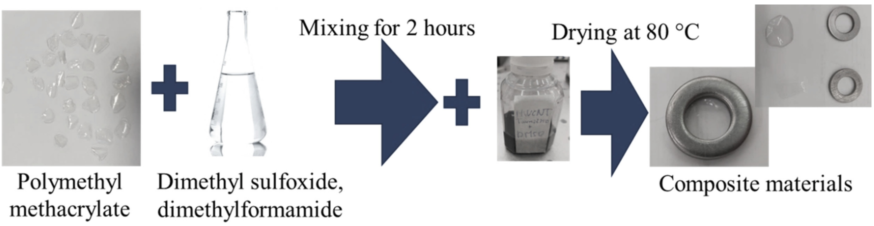

Fig. 3 Scheme for preparation of composites MWCNTs/Pc(**1**)

2.2 Spectral Measurement of the Materials Prepared

The absorption spectra of the prepared liquid dispersions of MWCNTs/Pc(**1**) in DMF, DMSO and distilled water were obtained (see Fig. 4).

Thin composites with high transmission (at least 78%) were obtained after adding dispersions with PMMA, mixing and evaporation of the solvent (Fig. 5). Measurements of solid and liquid samples with MWCNTs/Pc(**1**) indicate a low change in optical density in the range of 355–1064 nm, which indicates a small absorption of laser radiation in this range during linear interaction without the manifestation of nonlinear effects.

Raman spectroscopy is helpful for detecting lattice defects. In particular, it allows estimating the degree of defectiveness. It has been established initial CNTs defectiveness.

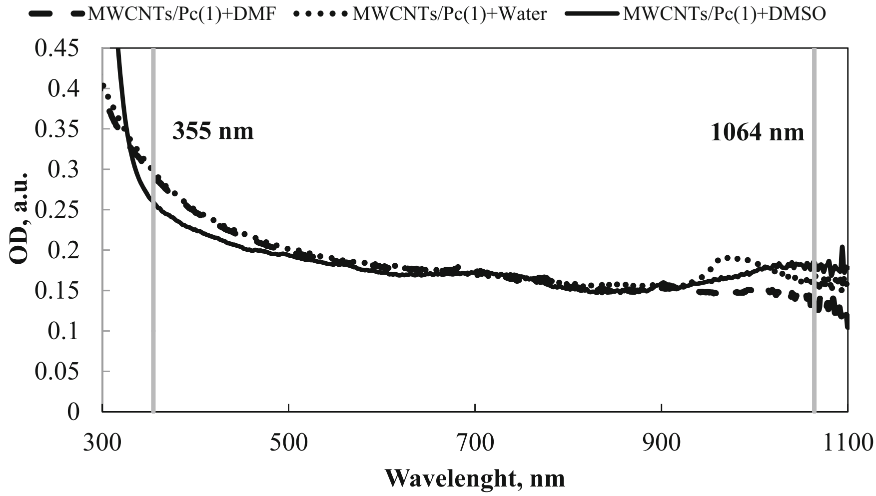

Fig. 4 Absorption spectra of liquid dispersions MWCNTs/Pc(**1**)

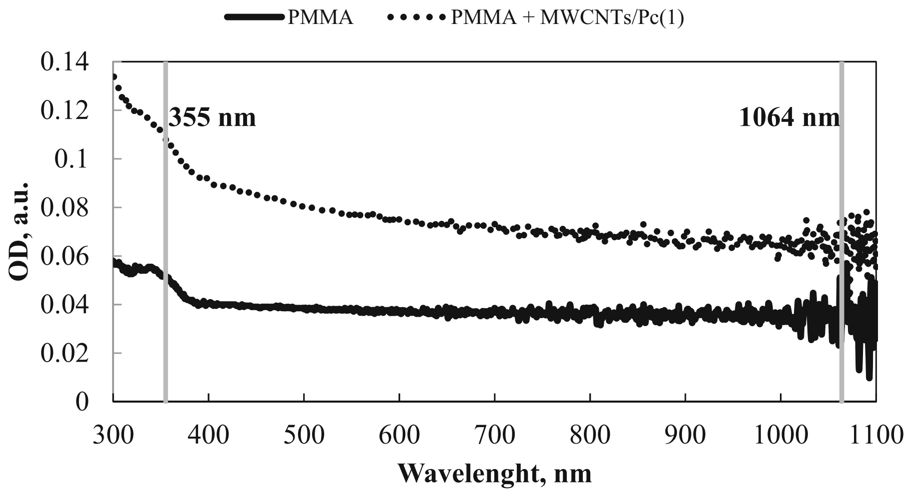

Fig. 5 Absorption spectra of composites MWCNTs/Pc(**1**)

The Raman spectra of obtained samples include bands G and D, G' and a D + G (Fig. 6), which are analyzed for identification CNTs [8]. It does not register RBM band, which is typical for single-walled CNTs [9], that confirms the use MWCNTs in our research.

2.3 Nonlinear Properties of Optical Limiting

On the basis of the radiation transport equation (RTE), the intensity of laser radiation can be determined in an optically thick material [6, 10]. Knowing the changes in the intensity of laser radiation, it is possible to determine the total energy of a single pulse, which is

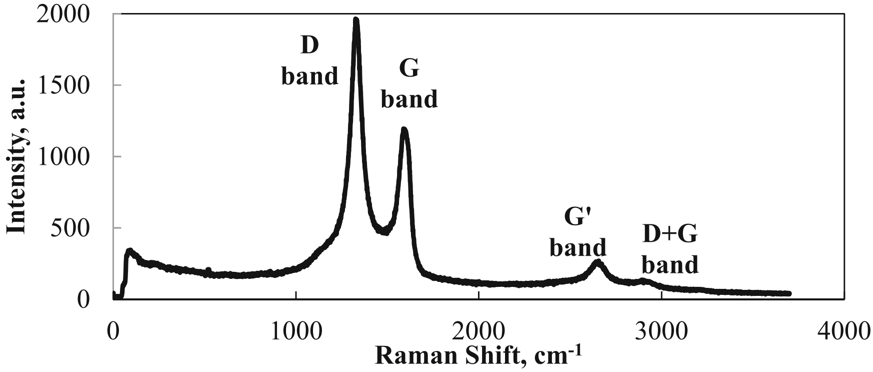

Fig. 6 Raman spectra of MWCNTs

determined experimentally using commercial energy sensors. To determine the optical limiting parameters, Nd:YAG laser source LOTIS TII was used. The laser setup was presented in previous work. The samples were exposed to pulsed laser radiation with a single pulse duration of 16 ns at a visible wavelength of 532 nm. MWCNTs/Pc(**1**), used in the composition liquid dispersions and solid composites, were studied by Z-scan and fixed location of material on the experimental setup (Fig. 7).

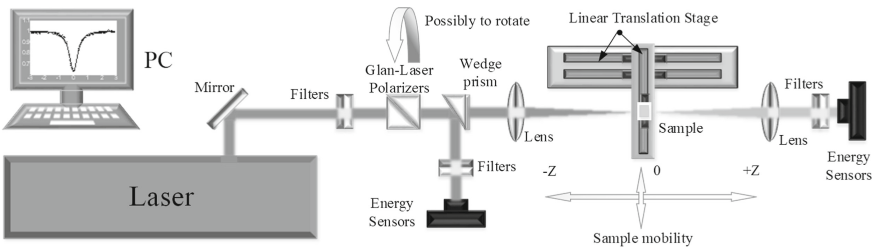

Fig. 7 Scheme of setup for studying optical limiting parameters

3 Results and Discussion

The results of the Z-scan with an open aperture for samples with MWCNTs/Pc(**1**) are obtained. Liquid dispersions demonstrated lower values of the normalized transmission (Fig. 8). For all data on optical limiting properties, solid lines show theoretical values. Experimental data are denoted with markers.

The data, measured by the method of fixed location of the samples at the focus of the lens, show that the boiling point of the solvent does not play a major role in optical limiting (Fig. 9). DMF has a higher boiling point than water, and the nonlinear response is stronger precisely in the case of this solvent. The main contribution is determined by the properties of the particles or molecules in the dispersions.

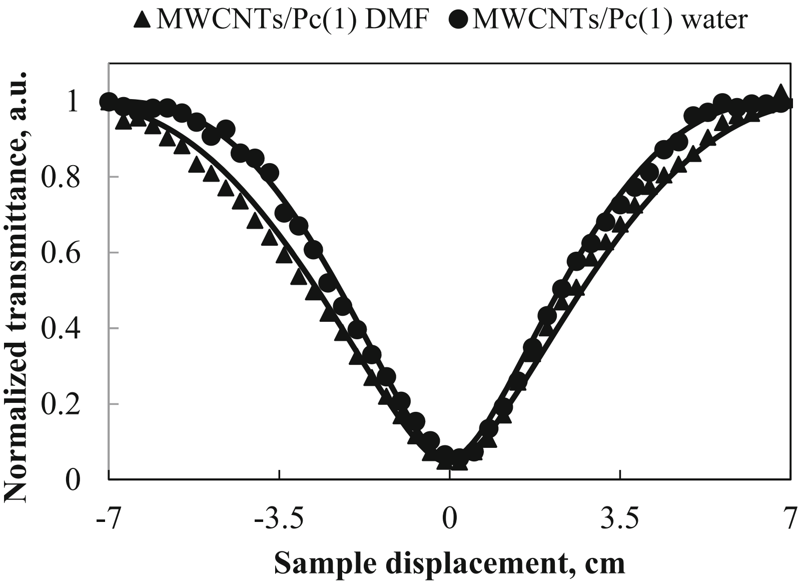

Fig. 8 Data of Z-scan with open aperture for dispersions of MWCNTs/Pc(**1**)

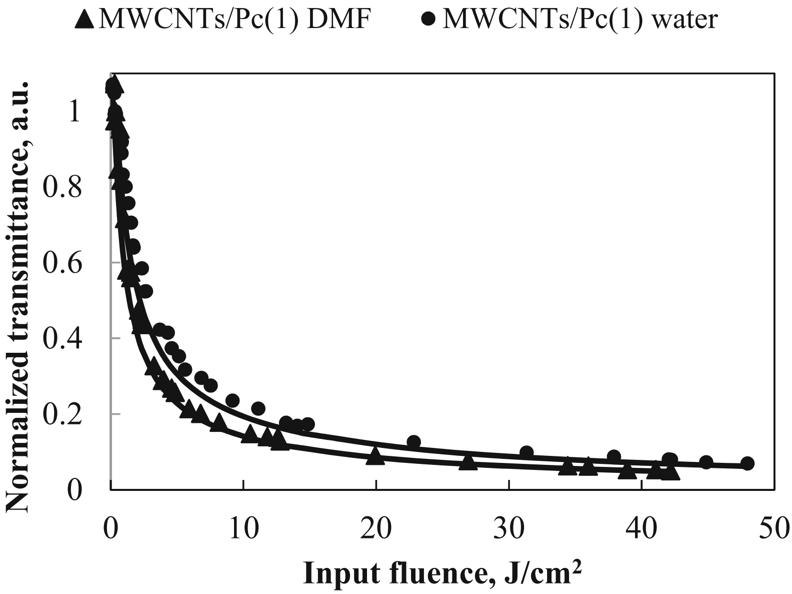

Fig. 9 Data of method of fixed location for dispersions of MWCNTs/Pc(**1**)

In accordance with the chosen method, a solid sample of the MWCNTs composites has a higher transparency than dispersions. In this case, even such a number of CNTs in a PMMA matrix is sufficient to obtain a significant nonlinear attenuation of radiation for optical limiting (Fig. 10).

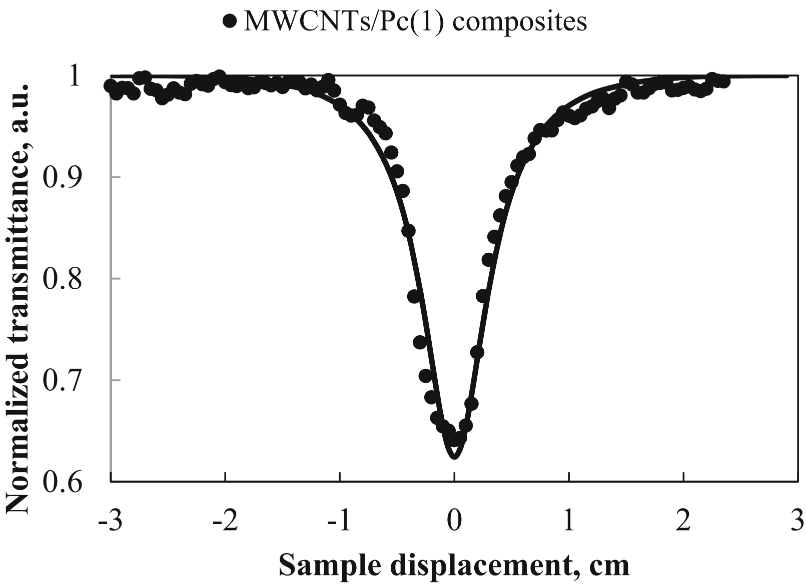

Fig. 10 Data of Z-scan with open aperture for composites of MWCNTs/Pc(**1**)

Based on the Z-scan data, the nonlinear optical parameters were determined and the theoretical values were calculated for the case, where the composites are located in the position of the lens focus (Fig. 11).

The results, presented in Table 1, indicate the different optical limiting properties of MWCNTs/Pc(**1**) in water and DMF. Such an effect may first be associated with the formation of ropes, such an effect is due to the properties of the solvents that are used.

With the same transparency as liquid dispersions, the composites show less attenuation of radiation and begin to reduce the transmitted power at a higher optical limiting threshold. Despite this, film limiters are more suitable for practical use in means of protection against laser radiation. The main purpose of the obtained functional nanomaterials is the ability to attenuate high-intensity laser radiation without damaging the sensitive elements of electro-optical systems and organs of vision.

4 Conclusions

Solid samples were prepared from liquid dispersions containing MWCNTs/Pc(**1**) and granular PMMA in DMF and DMSO at ~80 °C. Liquid dispersions with MWCNTs/Pc(**1**) demonstrate optical limiting of laser radiation, while the attenuation of laser radiation is

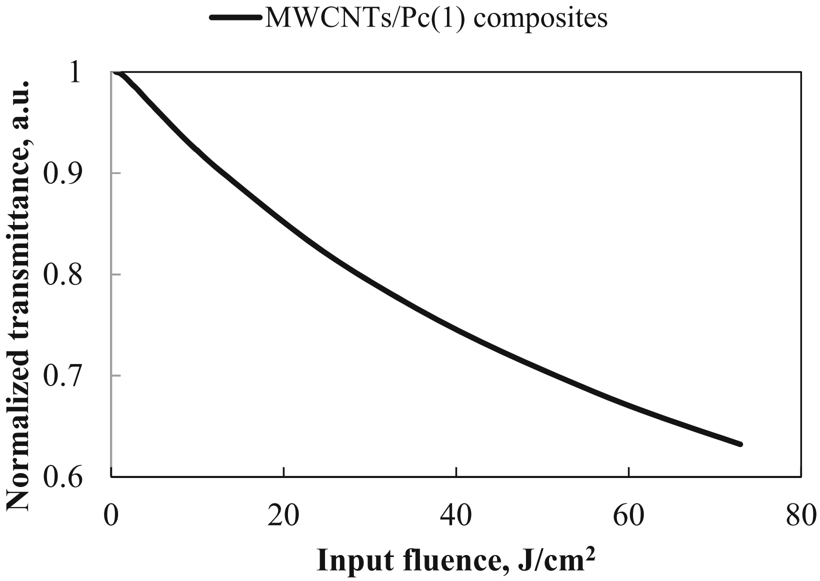

Fig. 11 Data of method of fixed location for composites of MWCNTs/Pc(**1**)

Table 1 Obtained MWCNTs/Pc(**1**) materials

Sample	U, μJ	I_0 GW/cm^2	d, cm	α, cm^{-1}	w_0, μm	β, cm GW^{-1}	I_{lth} MW/cm^2
PMMA composites with MWCNTs/Pc(**1**)	590	2.5	0.02	3.6	20.5	47	18.2
DMF dispersions with MWCNTs/Pc(**1**)	500	1.6	0.20	2.6	28.5	863	5.4
Water dispersions with MWCNTs/Pc(**1**)	500	1.9	0.20	2.1	27.7	514	7.6

determined not so much by the characteristics of the solvent as by the concentration and association of MWCNTs/Pc(**1**). Composites and dispersions with MWCNTs/Pc(**1**) can be used as the absorbing medium for optical limiting. Composites have lower nonlinear absorption and darken irreversibly at high intensities, while they can be manufactured with a thickness of less than 1 mm. Dispersions and composites have limited laser radiation resistance, but their replacement is much cheaper than a photosensitive matrix.

Acknowledgements. The research concerning synthesis of functionally substituted Pc(**1**) bearing a cycloctriphosphazene moiety adsorbed on the surface of MWCNTs was carried out with the financial support of the Russian Science Foundation (Grant 21-73-20016). The main research concerning protection of electro-optical systems and organs of vision with using composites MWCNTs/Pc(**1**) due to optical limiting was supported by the Ministry of Industry and Trade of the Russian Federation (State contract No. 20411.1950192501.11.003 from 29.12.2020, identifier 17705596339200009540).

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