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Nano-carbon in a hydrogel matrix for nonlinear optical applications

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ABSTRACT

We report on the optical power limiting properties of nano-sized carbon (single walled carbon nanotubes and carbon black) embedded in an aqueous-polymer matrix in the phase state of a hydro-gel. A polymer employed is Pluronic F-127, who simultaneously features as a stabilizer of the nano-carbon in a fluid water-polymer medium. Limiting thresholds of the composites are given in a bijection with a phase diagram (determined by DSC, rheometry and vibrational viscometry) of a matrix alongside its viscous characteristics and caloric properties of phase transitions involving the gel and micellar solution. Reversible gel-to-isotropic fluid transition of the matrix renders optical material thermo-healing with regard to optical breakdowns inflicted by high-intensity laser irradiation in the solid-like gel state.

1. Introduction

During recent years perspective applications for optically transparent condensed systems containing various nano-particles (nano-carbon, nano-metals, quantum dots, *etc.*) have been developed, *i.a.* non-linear optical power limiting (OPL) [1]. OPL consists in a drastic attenuation of light upon propagation through a material provided an incident light intensity surpasses a critical value termed a limiting threshold. This phenomenon is anticipated to be used for protection of sensors and the human eye against high intensity laser irradiation. The protecting OPL devices should comply with a number of requirements, *viz.*: optical transparence to low intensity light; sensitivity and fast non-linear response to an intense light irradiation; sufficient phase stability in the working environment and resistivity regarding disruption by high intensity irradiation.

Investigation of the nano-carbon OPL properties is closely related to a search for a dispersing medium appropriate for the specific use. Recently, fluid aqueous suspensions of nano-carbon have been extensively studied and applied [2,3]. Different kinds of films [4], crystalline colloidal arrays [5] and glasses [6,7] have also been reported to be germane matrices for photo-active particles. However, there are some issues with a design of practical optical materials operating with high-intensity radiation: *viz.*, fluid-state ones are not universally relevant for practical use, whilst, on the other hand, in the solid-state material there evolve incurable disruptions in the vicinity of a focal volume of high-intensity laser beam, thereby protective properties of the system are handicapped therein.

In the present investigation we gave a go to sort out drawbacks of the said phase states of the matrix, employing aqueous suspensions of either single-walled carbon nano-tubes (SWCNT) or carbon black (CB) suspensions, dispersing media being made rigid by Pluronic F-127 so as to provide the hydro-gel. This amphiphilic polymer also featured as a stabilizing micro-environment for nano-carbon in water [8–10]. It is also worth mentioning that gel materials based on Pluronic F-127 are so viscous and stiff that even heavy particles can be suspended without subsidence on a long time-scale [11–13].

Pluronics are nonionic tri-block copolymers poly(oxyethylene)-poly(oxypropylene)-poly(oxyethylene) [$(EO)_m(PO)_n(EO)_m$] with surfactant functionality [13–16]. Aqueous solutions of Pluronic F-127 have the simplest phase behavior and have been investigated by a number of techniques, including rheometry [11–13], small-angle neutron scattering (SANS) [12,13], differential scanning calorimetry (DSC) [13,15,17], light scattering (LS) [17], *etc.* A phase diagram as it comes from a number of sources is given in Fig. 1. It is

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ascertained that in dilute solutions and at low temperatures Pluronic F-127 exists in the form of free unimers. Above a certain temperature it aggregates into micelles owing to changing $(PO)_n$-part conformation which causes an increase of hydrophobicity of the latter [18]. With a further increase of temperature spherical micelles composed of hydrophobic $(PO)_n$ core and hydrophilic $(EO)_m$ corona form an optically transparent hydro-gel [11,19,20]. The hydro-gel formed is two-fold thermo-reversible: it undergoes an isotropic solution-to-gel transition on the lower boundary of the gel domain in the phase diagram and a re-entrant transition to a phase state with viscosity lower than in the gel, thereby resembling a liquid-like one at higher temperatures [11,14]. Formerly hydro-gels have been employed as matrices for the OPL materials quite seldom. In Ref. [21] chitosan hydrogels are reported to posses self-healing abilities of structural defects caused by laser irradiation. However, this property is inherent to materials with low volume fraction of the polymer (ca. 2%), the system being almost a liquid. This defines low mechanical, thermo-optical and strength characteristics of the material. In the work [22] graphene sheets were embedded in hydro-gel of polyvinyl alcohol, healing of the system after an optical damage was attained by heating it up to the temperature of 60–80°C and conversion into liquid with subsequent reverse transition into the gel.

Following the state-diagram of the water – Pluronic matrix [13,17,19] we processed gel-state suspensions of SWCNTs and CB and studied their OPL characteristics (a limiting threshold, a limiting factor and a break-down intensity) alongside possible rejuvenation of the OPL functionality by temperature-induced phase transitions into isotropic liquid suspensions. The property of hydro-gel thermo-reversibility casts scenarios for processing prototype solid self-healing materials, which can be used in various optical applications. Note in passing, regeneration of purpose functionality of optical materials also stands in the field of optical data storage [23].

2. Materials and methods

The tri-block copolymer, Pluronic F-127 ($M_w = 12.6 \cdot 10^3$) was purchased from Sigma Aldrich and used as received. It is stated that,

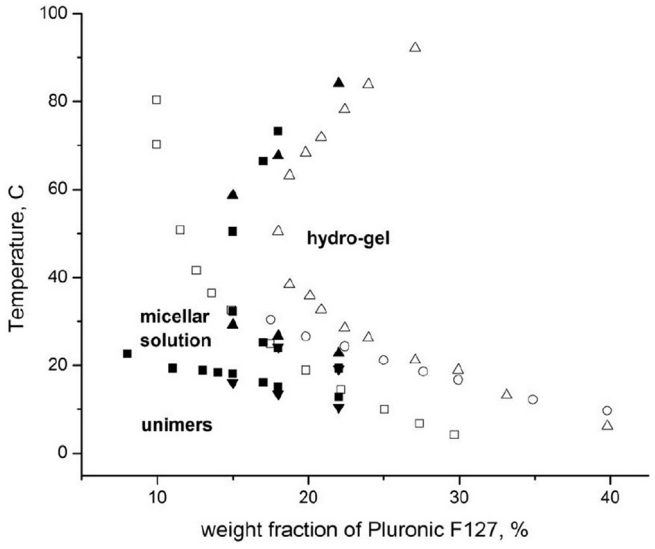

Fig. 1. Phase diagram of Pluronic F-127 in water. Open signs are data from literature [17]: – circles [13], – squares [19], – triangles. Filled signs designate the data of the present study: DSC – triangles (vertices down), viscometry – squares, rheometry – triangles (vertices up).

take away some properties (*e.g.*, surface tension), the fractionalized and the un-fractionalized samples of this polymer have virtually the same phase behavior [24]. We used distilled water for processing aqueous polymer mixtures, because it has been shown [18], that whether it is D_2O or a distilled H_2O, neither gelation nor micelization lines in the state space of a binary system are affected.

We used CB (Carbon nano-powder from Sigma Aldrich, purity claimed by a Producer > 99%), whose crystallites had linear dimensions not surpassing 50 nm. HiPCO SWCNTs were purchased from Carbon Nanotechnologies Ink., Houston, TX, with purity 85%. To process suspensions, a weight dose of Pluronic F-127 (5 wt%) for stabilizing nano-carbon was placed in water, wherein certain amounts of nano-particles (SWCNTs or CB) were added: SWCNTs – 0.03 wt%, CB – 0.3 wt%. Blends gotten underwent ultra-sonic processing: the power of a tip employed was *ca.* 1 kW, a regime of processing included two periods of 15-min duration with 15-min break between them. Ultra-centrifugation was performed differently for suspensions with different nano-particles: SWCNT suspensions were processed with Sorvall WX Ultra Series (Thermo Scientific; rotor T 890, 50000 rpm, 1 h duration), CB dispersions with LMC-4200R (Biosan, Latvia; 4000 rpm, 20 min duration). Supernatants for preparing samples were taken in both cases as 2/3 of the total vial volume (4 ml). This sort of mechanical processing ensured removal of catalysts remnants and admixtures of alternative allotropic carbon modifications from the samples, also providing higher fractions of isolated nano-tubes, their smaller fine bundles and smaller particulars of CB. Our previous Cryo-TEM monitoring of the mechanical processing impact on the degree of SWCNT aggregation in the suspensions stabilized by common surfactants [25] indicated that using of the aforementioned ultra-sonication/ultra-centrifugation procedure ensured an average diameter in the SWCNT populace of the feed suspensions equaling to *ca.* 2 nm and a contour length – *ca.* 150 nm. As it concerns the size of CB particulates, dynamic LS (Zetasizer Nano ZS, Malvern Instruments) observations showed distribution of nano-carbon particles in the interval 40–50 nm. In the present work we did not set a specific assignment of varying the size of nano-carbon in transparent condensed-state matrices with an aim to get its correlation with OPL parameters, insofar as principal phenomenology of this dependence in SWCNT dispersions was addressed in our previous work [3]. Main trends concerning non-linear optical effects in fluid suspensions containing CB particles with varied sized were also discussed elsewhere [26,27]. Preparation of the gel-forming compositions consisted of mixing weighed amounts of the polymer and water followed by allowing equilibration for about a week depending on the copolymer concentration at temperatures +4 – +6 °C. Then an appropriate dose of carbon nano-material suspension was added to the system obtained. After stirring, the tubes were kept in a refrigerator for a couple of days before measurements.

Characterization of suspensions and hydro-gels containing nano-carbon was performed by absorption spectroscopy (Lambda 950 Perkin Elmer, quartz cuvettes, path length 1 cm, wavelength interval 250–900 nm). Fig. 2 exemplifies the obtained spectral lines of hydro-gels. For the SWCNT system one can easily distinguish peaks corresponding to the band-gap optical transitions, characteristic for the HiPCO nano-tubes [28]. Spectrum of CB gel shows smooth broadband absorption. Maxima ($\lambda \approx 270$ nm) for gels with both morphologies correspond to π-π^* molecular orbital transition, intrinsic to sp^2 hybridized carbon bonds.

As is seen in Fig. 1, there is no complete consistence regarding location of the state domains in the phase diagram "Water + Pluronic F-127" between the sources [13,17,19]. Discrepancies may stem from a number of origins, *viz.*, a batch of the polymer, its molecular mass, peculiarities of methodologies