Optical study of composite material with nanosized fullerenol inclusions

A E Karpunin¹, I V Pleshakov¹,², O V Proskurina³, V I Gerasimov², A A Nechitalov², N V Glebova², A V Varlamov¹,² and M V Parfenov¹,²

¹Peter the Great Saint Petersburg Polytechnic University, St. Petersburg, 195251, Russia
²Ioffe Institute, St. Petersburg, 194021, Russia
³Saint Petersburg State Institute of Technology (Technical University), St. Petersburg, 190013, Russia

E-mail: alphadunce@gmail.com

Abstract. A composed material in the form of polymer matrix (polyvinyl alcohol) with imbedded nanoparticles of polyhydroxylated fullerene (fullerenol) was studied by optical methods. The host material was selected as a convenient media with such properties as flexibility, optical transparency and water solubility, which was utilized for films fabrication. The samples obtained were investigated by visible and infrared spectroscopy, and also the light scattering was examined at different wavelengths. It was shown that at high concentration of filler it forms clusters with sizes of about tens of nanometers, which is consistent with the data of other works.

1. Introduction

There is a diversity of inhomogeneous media with different micro- and nanosized inclusions which are promising for such areas as, for example, electronics, photonics, medicine and others [1-3]. Among them the carbon containing composite materials are of special interest owing to their applicability for optoelectronic devices and challenging physical properties. The possible carbon substance which can be impregnated into a base material to originate such a composite is a water-soluble fullerene form - polyhydroxylated fullerene or fullerenol, attracting now a great attention of investigators [4]. This compound have general formula C₆₀(OH)ₙ, where n depends on preparation conditions, and modification of the surface of fullerene molecules by hydroxyl groups provides water dissolution.

In this work the system comprised of polyvinyl alcohol (PVA) as a matrix and polyhydroxylated fullerene as an imbedded admixture was investigated. A number of studies on similar compositions, carried out recently [5, 6], demonstrated their unusual behavior. It should be mentioned that this substances are convenient in utilization because of their transparency in a wide range and mechanical flexibility, also being practical in preparing due to solubility of PVA in water.

An important question here is what the manner in which fullerenol embed into host polymer and what structure it forms there. One of the methods, used to solve this problem, was nuclear magnetic resonance (NMR) [7], which was applied to the study of composite with high fullerenol concentration (the latter was necessary to provide an intense NMR signal). It was shown by observation of NMR peaks typical for the bulk material that the filler tend to assemble into clusters. The goal of present work was to investigate the state of fullerenol in PVA using optical technique, applied to the same
samples. The infrared spectroscopy provides information on molecular groups, and comparing the spectra, obtained for bulk and impregnated fullerenol can define the peculiarities of the latter. Being added by spectroscopic measurements in visible, these data present complete information on optical properties of the samples in a wide range. The scattering of light (at different wavelength) can be utilized for estimation of characteristic size of inhomogeneities, and, as it is known, it is effective for the analysis of macromolecules, molecular associates and highly dispersed particles [8, 9]. The mentioned methods were used in present work as a complex optical approach to study PVA/fullerenol composites.

2. Samples and experimental methods

2.1. Samples preparing and characterisation

The samples were prepared by drying of commixed water solutions of PVA and polyhydroxylated fullerene.

The precursor was made by the procedure described in [10], which consisted in preparing of fullerene C\textsubscript{60} by graphite electrodes erosion in an electric arc, separation and purification of C\textsubscript{60} in a chromatographic column, and subsequent synthesis of fullerenol with benzene and sodium hydroxide. The obtained material was tested by X-ray photoelectron spectroscopy, thermal and elemental analyses. It was shown that the synthesized substance corresponds to fullerenol with specified formula C\textsubscript{60}(OH)\textsubscript{42}·4H\textsubscript{2}O.

The composite was fabricated from the mixture of 5 wt. % of water PVA solution and fullerenol solution with concentration of 50 mg/ml (it is close to the limiting value [11]). The blend was carefully interfused at room temperature or at 90\degree C (there was no experimentally observable differences for these variants), deposited onto the glass substrate and then dried, forming the films with thicknesses of 30-60 \( \mu \)m.

2.2. Optical experiments

The infrared measurements were carried out by spectrophotometers IRTracer-100 (Shimadzu), and measurements in visible by Specord 210 (Analytik Jena). Because of particularity of the experimental facilities the results of the former were presented as transmittance spectra and of the latter as optical density dependence on wavelength.

The scattering was investigated by the standard setup: the laser beam with vertical polarization was directed normal to the sample surface (two wavelength \( \lambda \) were used, \( \lambda = 532 \text{ nm} \) and \( \lambda = 632.8 \text{ nm} \)) and the scattered radiation of vertical and horizontal polarizations was registered by photodetector at different angles \( \theta \) in horizontal plane.

3. Results and discussion

Figure 1 demonstrates the infrared spectrum of a composite sample, which practically represents a combination of separately measured corresponding dependencies for PVA and bulk fullerenol [12]. The absorption peaks in the interval of 900 – 2000 cm\(^{-1}\) are very similar to those which have been obtained for the latter, except of weakly pronounced peculiarities, marked in figure 1 by arrows (in spite of weakness of the effect it was reproducible for a number of samples). Most of them were attributed to the molecular vibrational modes, and their conservation in the composite material points to presence of the fraction of pure fullerenol. Some authors observed an additional peak at 1720 – 1730 cm\(^{-1}\) for a specially processed bulk samples [12], ascribing it to the influence of carbonyl groups. In our case the analogous action from the matrix at the phase boundary can be supposed.

Because the existence of fullerenol clusters should be apparent in a wide interval of wavelengths, the experiments in visible range also were carried out. In figure 2 the results of spectral measurements in visible are shown, figure 3 demonstrates the scattering data, obtained with red and green lasers. The curves in figure 2 cannot be described only by a dependence of \( 1/\lambda^4 \)-type; so, it should be accepted that the scattering and absorption at \( \lambda \approx 400 – 800 \text{ nm} \) present simultaneously. In agreement with [13]
the scattered light has both vertical and horizontal polarizations. It may suggest the nonspherical form of clusters, but the details of the phenomenon we leave for future discussion. Taking into account the data of [13] it was possible, by the relation $U(180^\circ) / U(0^\circ)$ obtained for two wavelength (see figure 3), estimate roughly the characteristic size of scattering center. For the spherical approximation of its shape its diameter turned to be of about 50 – 100 nm. Thus, the number of molecules in a cluster
should be of the order of $10^4 - 10^5$, with their amount at the surface of few percent. It means that in the case of high concentration, the imbedded fullerenol forms sufficiently large particles, which behaves like a bulk substance.

4. Conclusion
In this work we used a number of optical methods to test the properties of composite material PVA/fullerenol. It was shown that for the concentration, close to the limiting one, it forms nanosized clusters. The result is consistent with data of NMR.

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