PHYSICS OF NANOSYSTEMS

ON THE CONTROLLABLE CHANGE
OF THE REFRACTIVE INDEX OF A SILICONE POLYMER

V.I. GRYGORUK, A.N. DMYTRUK, V.M. OGENKO[1], YU.T. ONYS'KO, YU.A. SLINCHENKO

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Taras Shevchenko Kyiv National University, Faculty of Radiophysics
(6, Academician Glushkov Ave., Kyiv 03127, Ukraine; e-mail: ys@univ.kiev.ua),

[1]**V.I. Vernadsky Institute of General and Inorganic Chemistry, Nat. Acad. Sci. of Ukraine**
(32/34, Academician Palladin Ave., Kyiv 03680, Ukraine)

Specific materials that include silica nanoparticles have been investigated. A possibility for the refractive index of a silicone polymer to be controlled within the limits from 1.4062 to 1.4090 at a temperature of 18°C has been demonstrated.

Polymers which are in use today for fabricating films, multilayered structures, and optical fibers (OFs) have definite discrete values of refractive indices, with an opportunity to vary the latter smoothly being absent [1]. But for modeling new materials and producing, e.g., special OFs and OF elements, the materials are needed which allow their refractive index to be controlled in the course of their fabrication.

In this work, we have studied special materials which include silica nanoparticles [1,2]. A SIEL polymer (a standard polydimethylsiloxane elastomer) which is widely used, in particular, for manufacturing OFs was selected as a parent substance. In order to change the index of refraction, we used nanoparticles of silica with

dimensions from a few to tens nanometers as fillers [3, 4]. The choice of just such fillers was brought about by the necessity to obtain, as a result, an optically transparent composite with the physical properties similar to those of the pure polymer (the particle sizes of the filler were much smaller than the light wavelength). In this work, we have studied the following fillers: A1 — an aerosil with the specific surface of 50 m^2/g and the characteristic average dimension of particles of 80 nm; A2 — an aerosil with the specific surface of 180 m^2/g with attached $Si(CH_3)_2$-radicals (the hydrophobic surface) and the characteristic average dimension of particles of 5 nm; A3 — an aerosil with the specific surface of 380 m^2/g with chemisorbed OH-radicals (the hydrophilic surface) and the characteristic average dimension of particles of 2 nm [5–7].

Preliminarily investigated were the transmission spectra of the fillers, the pure polymer, and their composites. One can see (see Figs. 1 and 2) that if filler
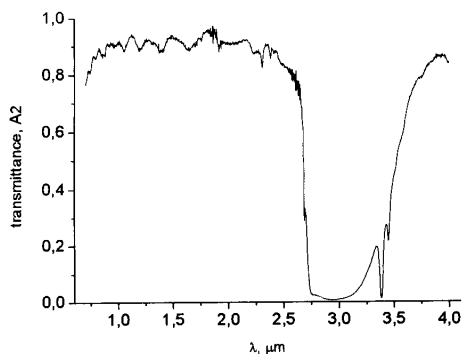

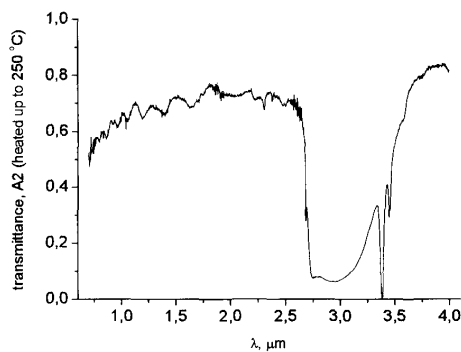Fig. 1. Transmittance spectrum of filler A2

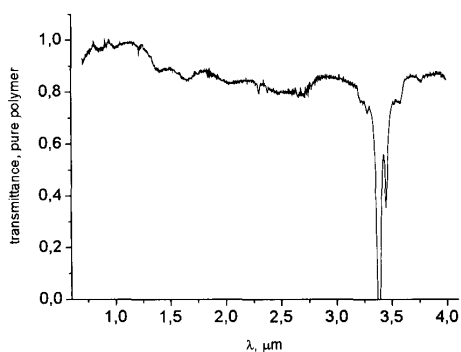Fig. 2. Transmittance spectrum of filler A2 heated up to 250°C

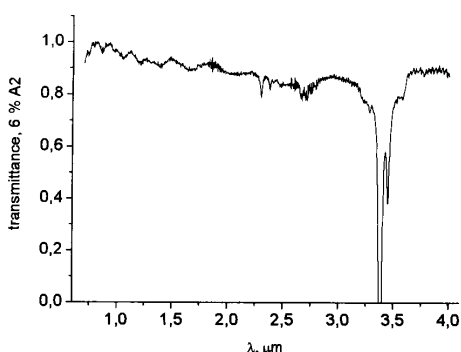Fig. 3. Transmittance spectrum of the polymer without any filler

Fig. 4. Transmittance spectrum of the polymer with filler A2; the filler concentration is 6 wt.%

A2 was heated up to 250°C, its transmission spectra within the wavelength range 1.0—2.5 μm remained practically unchanged. The analogous regularities were also observed for the other fillers, which differ by the chemistry of their interfaces and the amount of water absorbed on the surface. The presence of a filler in the parent polymer even at a significant concentration (the maximal concentration was 10 wt.%) practically did not affect the transparency of the specimens. Really, Figs. 3 and 4 testify to that the transmittance of the composite differs little from that of the parent polymer in the wavelength range indicated above.

The difference between the refractive indices of the composite and the pure polymer is defined by the concentration of a filler. Since the composite is similar, by its structure, to well-studied colloid solutions, we used the empirical dependence of the form [8]

$$n = n_0 + a_1 c + b_1 c^2 + ..., \qquad (1)$$

where n_0 is the refractive index of the pure solvent, and a_1 and b_1 are constants $(a_1 \gg b_1)$, to describe the dependence of the refractive index of the composite n on the filler concentration c. The experimental dependences
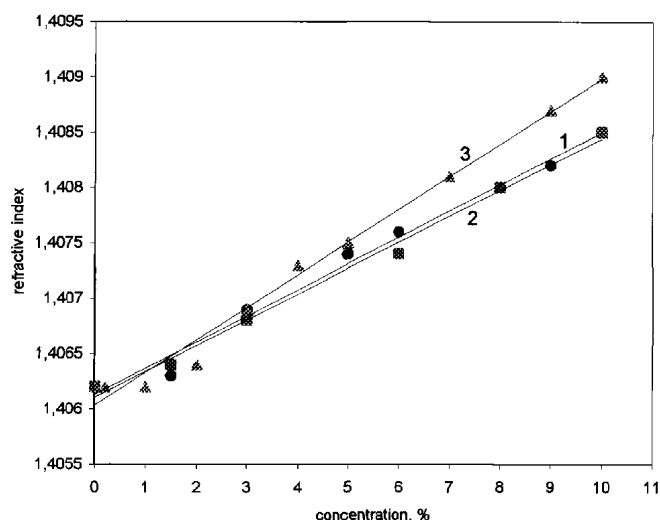

Fig. 5. Dependences of the refractive index on the filler concentration for various fillers: A1 (*1*), A2 (*2*), and A3 (*3*)

$n(c)$ are shown in Fig. 5. The refractive indices of the composites were measured at a temperature of 18°C. Insignificant deviations from linearity may be explained, in particular, by the inaccuracy of the calculation of the composite concentration, which, in its turn, resulted from the errors made while determining the masses of components.

The authors' choice of the filler concentrations (no more than 10 wt.%) and, accordingly, the variation amplitudes of the refractive indices of composites was based upon the following considerations. First, the presence of the filler should not result in a substantial variation of the transmittance of the polymer itself. If the filler concentration increases to about 20 wt.% or more, light scattering becomes important, because filler particles become closer to one another (they become separated by distances of the order of the light wavelength λ). Secondly, the technological expediency requires that, for the relationship between the refractive index and the viscosity of the composite to be optimal, the filler concentration should not exceed 10 wt.%. If the filler concentration should grow further, the refractive index of the composite would approach, in the limiting case, that of quartz.

Owing to the action of adsorption forces, there are always polymer molecules between filler particles, which provide the optical contact for light to pass. The energy of the supramolecular interaction between the particles and the polymer is larger than the energy of the dispersion interaction between the particles themselves; therefore, the filler clusterization does not occur. Moreover, the authors specially modified chemically the
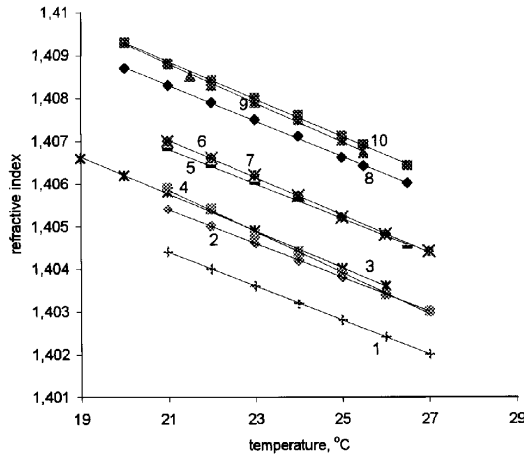
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Fig. 6. Temperature dependences of the refractive index of the pure polymer (*1*); of 5-wt.% composites with various fillers: A1 (*2*), A3 (*3*), and A2 (*4*); of 10-wt.% composites with various fillers: A1 (*5*), A2 (*6*), and A3 (*7*); and of 10-wt.% polymerized composites with various fillers: A1 (*8*); A3 (*9*); and A2 (*10*). Curves *6* and *7* coincide

surface of the filler [7] to minimize the interaction between the particles and to ensure the maximal interaction between the particles and the functional groups of the polymer in use (the phobic interaction). Such a situation was also preserved after the composite having been polymerized.

From the stated above, one might expect that a practically linear dependence of the refractive index of the composite on the filler concentration would be also observed for higher filler concentrations. It was confirmed in work [1].

It is known [8] that the dependence of the refractive index on temperature t at a not very high pressure is mainly defined by a variation of the substance density. A rather accurate calculation of n in a wide temperature interval can be made by using empirical dependences of the type

$$n = n_0 + a_2 t + b_2 t^2 + ..., \qquad (2)$$

where n_0 is a constant, and a_2 and b_2 are constant algebraic quantities, with $a_2 \gg b_2$. In a certain temperature range (up to 40 °C), this dependence is assumed linear. Experimental data are in a rather good agreement with linear dependences (see Fig. 6). It is evident that these dependences, within the measurement error which was 0.0001 for the refractive index at a temperature of -0.1 °C are linear and possess practically identical slopes. Provided a low pressure and not a very wide temperature interval, the variation of the refractive index is governed only by the variation of the substance density which is proportional, under such

conditions, to the refractive index [8]. So that, the data obtained are quite natural. Similar investigations [1] showed that the linear dependence is also preserved in a wider temperature interval, from -50 to 30 °C.

Thus, in this work, we have demonstrated an opportunity to control the variation of the refractive index of a silicone polymer. We have fabricated a polymer possessing the refractive index within the preassigned limits and have studied the temperature dependence of the refractive index of this polymer. A necessity for materials with predetermined refractive indices at given temperatures (in particular, for fabricating special quartz-polymer fibers, functional elements of fiber sensors, for optical, buffer, and protective sheaths of OFs, etc.) determines the urgency of the results stated above.

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ПРО КЕРОВАНУ ЗМІНУ ПОКАЗНИКА ЗАЛОМЛЕННЯ КРЕМНІЙОРГАНІЧНОГО ПОЛІМЕРУ

В.І. Григорук, А.М. Дмитрук, В.М. Огенко, Ю.Т. Онисько, Ю.А. Слінченко

Р е з ю м е

Виконано дослідження спеціальних матеріалів з наночастинками кремнезему. Показана можливість керованої зміни показника заломлення кремнійорганічного полімеру у межах від 1,4062 до 1,4090 при температурі 18 °C.