



Impact of inorganic nanoparticles on optical properties of low refractive index waveguiding polymers

LEONID M. GOLDENBERG,^{1,2}  MATHIAS KÖHLER,¹ OLAF KAHLE,¹
AND CHRISTIAN DREYER^{1,2,*}

¹Fraunhofer-Institute for Applied Polymer Research, Research Division Polymeric Materials and Composites PYCO, Kantstrasse 55, 14513 Teltow, Germany

²University of Applied Science Wildau, Hochschulring 1, 15745 Wildau, Germany

*christian.dreyer@th-wildau.de

Abstract: The objective of this work is to improve the optical properties of low refractive index polymers used for waveguide by introduction of inorganic nanoparticles. Copolymers of fluorinated monomers and glycidyl methacrylate are used. Introduction of SiO₂ nanoparticles into polymer matrix is performed by direct mixing; copolymerization with SiO₂ nanoparticles modified by monomer, and *in situ* sol-gel formation of SiO₂ during photochemical cross-linking and annealing catalyzed by photoacid generator. It is demonstrated that nanoparticles are able to decrease thermo-optic coefficient. It is also possible to fabricate waveguiding layers by direct introduction of nanoparticles without compromising of optical propagation losses.

© 2020 Optical Society of America under the terms of the [OSA Open Access Publishing Agreement](#)

1. Introduction

Low refractive index polymers are used as passive materials in planar waveguides [1–7] and optical fibers [8]. The main requirements to such polymers are low refractive index (1.5 or smaller), good processing properties, low birefringence of the films on a Si substrate, low optical losses, and ability to tailor thermo-optic coefficient (TOC) depending on application purposes. Low TOC is a requirement for passive optical waveguides. Both low refractive index and low optical losses at telecommunication wavelengths (around 1550 nm) are usually achieved by substitution of hydrogen atoms by fluorine and by avoiding where possible of O–H and N–H bonds, which have strong absorption at this wavelength. The required refractive index contrast between core and cladding polymers is attained by changing of the polymer composition. Organic or hybrid polymers [9] are usually used for this aim. However, a combination of inorganic and organic materials as nanocomposites for optical waveguiding materials has received little attention so far.

From the one hand, inorganic materials demonstrate considerably lower TOCs, since this parameter is linked to the thermal expansion coefficient. Some of them (*e.g.* MgF₂, CaF₂, AlF₃, SiO₂) possess also low refractive indices. The MgF₂ nanoparticles (NP) were introduced into polymer matrix [10,11] and they were able to decrease the refractive index of nanocomposites [10]. It was also demonstrated that introduction of SiO₂ NPs prepared by *in situ* sol-gel reaction was able to decrease refractive index of polyimides used for the fabrication of optical waveguides [12]. From the other hand, polymers often exhibit good film building properties, and the synergy of both materials combined into nanocomposites can be used for the fabrication of improved materials. Two of possible ways for nanocomposite fabrication are shown in Scheme in Fig. 1. Nanocomposite approach could be a suitable method for tuning optical properties of waveguiding materials. The change could be realized in the direction of reducing refractive index and TOC.

The impact of inorganic NPs on optical properties of the polymers is yet to be estimated. For example, fabrication of optical waveguides using polymer matrix filled with Au NPs has been

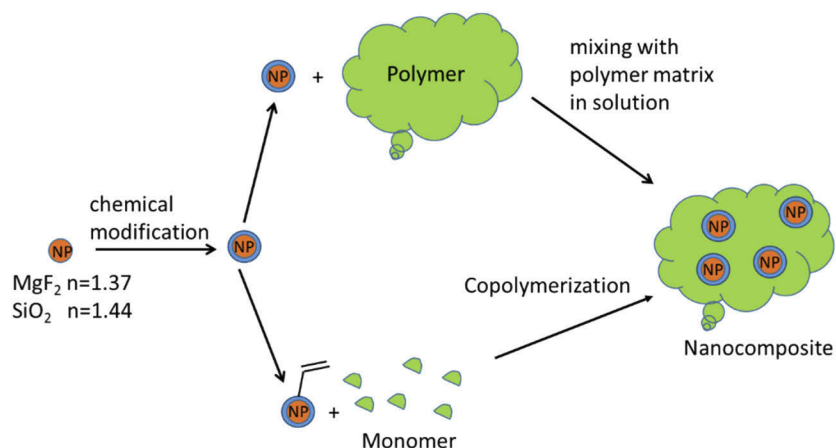


Fig. 1. Nanocomposite fabrication starting from NPs modification if required. Top way is direct mixing of NPs into polymer matrix in solution and bottom way is copolymerization of NPs modified by double bond together with other acrylate/vinyl monomers.

reported recently [13], but no information concerning optical losses was presented in this work. While influence of NPs on refractive index and TOC is theoretically clear [14], the influence of NPs distributed in polymer matrix on optical propagation losses is not well studied. Inorganic materials (core of a NP) have to decrease optical losses, but their organic shell, required for the compatibility with the polymer matrix, might increase optical losses depending on its chemical composition. In addition, possible scattering, arising when NPs are not sufficiently small or aggregate in the polymer matrix, will increase optical losses. Therefore, the impact of NPs on the optical losses has to be studied.

The goal of this work was to introduce SiO₂ NPs into polymer waveguiding materials and to investigate their influence on optical properties (refractive index, TOC, and propagation losses). The copolymers of pentafluorostyrene and glycidyl methacrylate, because of their low optical losses [15], were predominantly used as waveguiding materials. An introduction of other monomers in the polymerization mixture (fluorinated or chlorinated) was used to tune the refractive index of final polymer according to Scheme in Fig. 2.

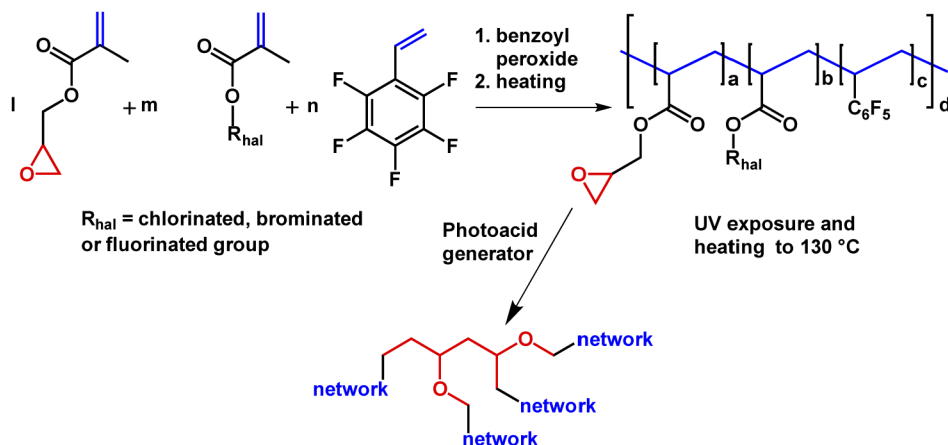


Fig. 2. Polymerization and photochemical cross-linking for fabrication of waveguiding copolymers.

2. Experimental

2.1. Materials and film preparation

Fluorinated and chlorinated monomers (ABCR), glycidyl methacrylate (Sigma-Aldrich), dioxane (Carl Roth), cyclopentanone (ABCR), 2-ethoxyethyl acetate (Fluka), nonafluorohexyltriethoxysilane (Fluorochem), 3-(trimethoxysilyl)propyl methacrylate (Sigma-Aldrich) were used as received. Benzoyl peroxide (Merck) was dried over CaCl_2 in vacuum desiccator. Silica nanoparticles (15–20 nm in diameter) in 2-butanone, toluene, and propylene glycol monomethyl ether acetate (PGMEA) were received from Nissan Chemicals Industries (Japan). Silica NPs Nyasil 5, HDS-3, DP5820, S125M were a gift from Nyacol Nano Technologies, Inc. (USA). Silica NPs modified with methacrylate, double bond, and porous silica NPs were purchased from IOLITEC (Germany). Silica NPs dispersions Nanopol were a gift from Evonik. The properties of silica NPs are collated in Table 1.

Table 1. Characteristics of SiO_2 NPs.

NP	Manufacturer	Diameter [nm]	Solvent	Functionalization
MEK-ST	Nissan	15-20	2-butanone	
PMA-ST	Nissan	15-20	propylene glycol methyl ether acetate	
TOL-ST	Nissan	15-20	toluene	
Nyasil 5	Nyacol	2		
HDS-3	Nyacol	70-80		
DP5820	Nyacol	20	ethylene glycol	
S125M	Nyacol	70-80		methacrylate
	IOLITEC	10-20		methacrylate
	IOLITEC	10-20		double bond
Porous	IOLITEC	10-20		
Nanopol C764	Evonik	20	methoxypropyl acetate	

For copolymer synthesis according to Scheme (Fig. 2), glycidyl methacrylate, pentafluorostyrene, trifluoroethyl methacrylate or other fluorinated or chlorinated acrylates (*ca.* 10 g), in dioxane (50 ml) with dibenzoyl peroxide (0.2 g) were purged with nitrogen for 15 min under stirring, then inserted in oil bath to achieve 80 °C inside, and maintained at this temperature for 6 h. After cooling, the solution was poured into water; the polymeric precipitate was separated, washed with ethanol, and dried at 50 °C in vacuum. Subsequently, the polymer was dissolved in a small amount of hot ethyl acetate and after cooling precipitated with EtOH and dried at 50 °C in vacuum. The monomer feeds corresponding approximately to the copolymer compositions (yield of polymerization was higher than 80% and we assume that the conversion of monomers was close to 100%) for copolymers used in this work are collated in Table 2.

Table 2. Copolymer composition according monomers feed (wt%).

Copolymer	Pentafluorostyrene	Glycidyl methacrylate	Trifluoroethyl methacrylate	Pentachlorophenyl methacrylate
Polymer 1	5	35	60	
Polymer 2	34	33	33	
Polymer 3	25	10		65
Polymer 4	90	10		
Polymer 5	25	35	40	
Polymer 6	20	15		65

Porous NPs (IOLITEC) were treated for modification by nonafluorohexyltriethoxysilane in *i*-PrOH in a presence of HCl at 90 °C. Similarly, the DP5820 nanoparticles from Nyacol were modified using 3-(trimethoxysilyl)propyl methacrylate. These NPs modified with monomer unit and other commercial NPs modified with double bond (S125M from Nyacol and others from IOLITEC, see Table 1) were used for the copolymerization with other monomers according to Scheme (Fig. 2), similarly as described above, leading to copolymers with NPs in the side chain (Fig. 1, bottom way and Fig. 3, top way). The incorporation of silica NPs in the polymer matrix in this case was proven by thermogravimetric analysis (TGA, *ca.* 20-30 wt.% of inorganic residue).

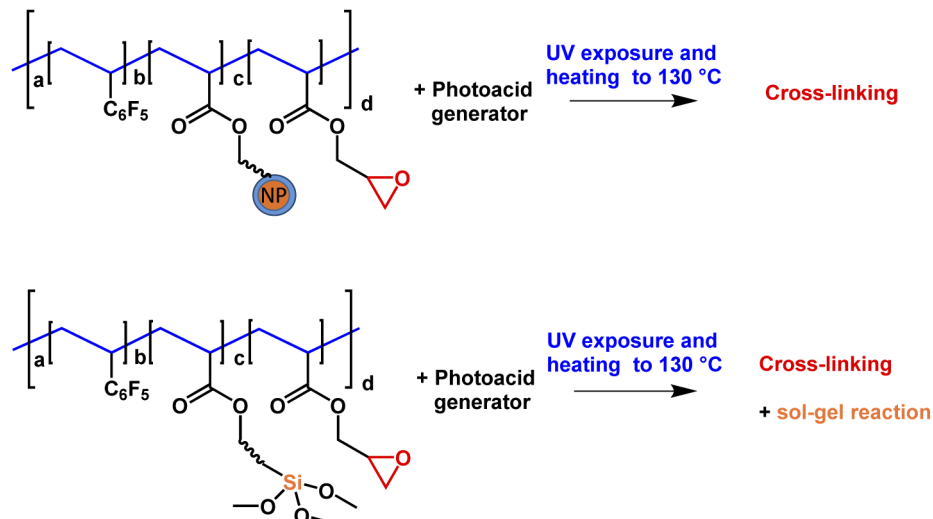


Fig. 3. Copolymer containing NPs as side chain (top way) and copolymers capable of *in situ* formation of SiO₂ NP by sol-gel reaction (bottom way).

The monomers were also copolymerized with 3-(trimethoxysilyl)propyl methacrylate leading to the copolymers used for *in situ* formation of NPs (Fig. 3, bottom way). These materials were used for the film formation without precipitation directly from synthesis solution in dioxane.

Commercial waveguiding material ZPU 480 (ChemOptics, South Korea) was received from C. Zawadzki (Fraunhofer Heinrich-Hertz Institute, Berlin).

Thin layers of polymers and nanocomposites were prepared by spin-coating using a P6700 spin-coater (Specialties coating system) or by casting onto Si wafer or fused silica substrate. The films were prepared from the mixtures of NPs and polymer and from polymers with NPs in the side chain in cyclopentanone or 2-ethoxyethyl acetate and from dioxane solution for *in situ* formation of NPs. All films were exposed to UV-light using an UV-H 200 mercury lamp (Panacol-Elosol) and then post-baked at 110-130 °C for cross-linking and sol-gel reaction for *in situ* formation of NPs.

2.2. Measurements

Optical properties of polymer films (refractive index and thickness, TOC, optical propagation losses) were measured using m-line spectroscopy performed on a Metricon MODEL 2010/M Prism Coupler System (Metricon Inc., USA) with polymer films on Si and SiO₂ substrate. Optical losses of the planar waveguides were measured by a technique involving measurement of transmitted and scattered light intensity as a function of propagation distance along the waveguide [16]. This technique has been also used recently for the characterization of other polymer optical waveguides [17–19]. Temperature dependent ellipsometric measurements were carried out using

a modified Sentech ellipsometer [20] with polymer films on Si substrates. TGA was performed using a Mettler-Toledo TGA 850 unit.

3. Results and discussion

Introduction of SiO₂ NPs into polymer matrix was performed in three different ways:

1. direct mixing of NP dispersion with polymer solution
2. copolymerization of SiO₂ NPs modified by monomers with other co-monomers
3. *in situ* sol-gel formation of SiO₂ during photochemical cross-linking and annealing catalyzed by photoacid generator [21].

Direct introduction of NPs into polymer matrix is illustrated in Fig. 1 (top way) and two other approaches are depicted in Fig. 1 (bottom way) and Fig. 3.

3.1. Direct mixing

NPs from Nissan Chemical Ind., Nyacol, IOLITEC, and Evonik were used for the direct introduction of SiO₂ NPs into polymer matrix (Table 1). The copolymers containing glycidyl methacrylate for following photochemical cross-linking were applied as a polymer matrix (Fig. 2). Such polymer possesses a relatively low refractive index and also relatively low thermo-optic coefficient (TOC), namely, $-(1.4-1.7) \times 10^{-4} \text{ K}^{-1}$ depending on composition (*e.g.* Polymers 1 and 2 in Table 3). Core polymers with refractive index 1.5 (prepared using chlorinated monomer) exhibited lower TOC, usually below $-1.0 \times 10^{-4} \text{ K}^{-1}$ (Polymers 3 and 4 in Table 3). We were able to introduce MEK-ST, PMA-ST, and porous SiO₂ NPs from IOLITEC in such polymers. Porous NPs were preliminary modified by fluorinated silane for this purpose. TOC measurements, especially using thermo-ellipsometry (layer thickness below 1 μm), allow to use thinner layers. Therefore, it was possible to investigate a number of different materials. The results of TOC measurements by ellipsometry (for layers up to 1 μm thick) and by m-line spectroscopy using Metricon system (for layers of 3-10 μm thick) are collated in Table 3. However, only NPs from Nissan allow preparation of relatively thick layers to attempt the measurement of optical propagation losses. Other nanocomposites exhibited relatively low solubility that prevents fabrication of sufficiently thick layers by spin-coating. In addition to copolymers, commercial liquid mixture for waveguide preparation ZPU 480 (ChemOptics, South Korea) and proprietary liquid acrylate mixture developed in PolyPhotonics Project were also used for comparison. These mixtures of monomers and NPs were also obtained by direct mixing of NP dispersion with liquid monomer mixture followed by photochemical cross-linking on a substrate.

The examples of ellipsometric and m-line measurements are presented in Fig. 4.

It seems that porous NPs have no significant impact on TOC. This contradicts to the literature data, where incorporation of mesoporous silica NPs into polyimide decreased TOC by a factor of 2-3 [22]. However, NPs from Nissan definitely show an influence on the TOC leading to a decrease of TOC as it should be expected from inorganic material. As a rule, SiO₂ NPs are amorphous. Higher reduction of thermal expansion coefficient (linked to TOC) was observed for crystalline and asymmetrical NPs [23–27]. TOC decrease is especially clear for the Polymer 2 while starting polymer has relatively high TOC ($-(1.5-1.7) \times 10^{-4} \text{ K}^{-1}$). To check this data further, the same NPs were introduced into commercially available waveguide material ZPU 480 and proprietary acrylate mixture. Both mixtures produce polymer layer with relatively high TOC. Distinctive decrease in TOC was also observed in these cases (Table 3). However, one can see from the Table 3 that NPs have no or little influence on the glass transition temperature (T_g) and glass transition temperature in nanocomposite is determined by the polymer matrix. This should be expected actually, *e.g.* it was demonstrated for two polymer matrices experimentally and theoretically [28] that introduction of SiO₂ NPs into polymer matrix increases T_g by 10 °C only.

Table 3. Thermo-optic data for the nanocomposites obtained by direct introduction of NPs.^a

Material	Ellipsometry		m-line spectroscopy	
	TOC [10^{-4} K^{-1}]	T_g [$^{\circ}\text{C}$]	TOC [10^{-4} K^{-1}]	T_g [$^{\circ}\text{C}$]
Polymer 1 + 53wt.% MEK-ST	-1.1	90	-0.6 (-1.2)*	100 (90)*
Polymer 1 + 40wt.% MEK-ST			-0.55 (-1.4)	100 (90)
Polymer 2 + 60wt.% MEK-ST	-1.1 (-1.7)	not detected	-1.0 (-1.5)	not detected
Polymer 3 + 25wt.% MEK-ST			-0.7 (-0.65)	130 (130)
Polymer 4 + 30wt.% MEK-ST			-0.85 (-0.75)	110 (100)
Polymer 1 + 50wt.% porous NP modified	-1.25	100	-0.8-1 (-1.2)	100 (90)
ZPU 480 + 30wt.% MEK-ST	(-1.7)	not detected	-0.9 (-2)	not detected
Proprietary acrylate mixture + 30wt.% MEK-ST			-0.85 (-1.7)	60 (60)

^a*data for unfilled polymer matrix are in brackets, polymer composition is in Table 2

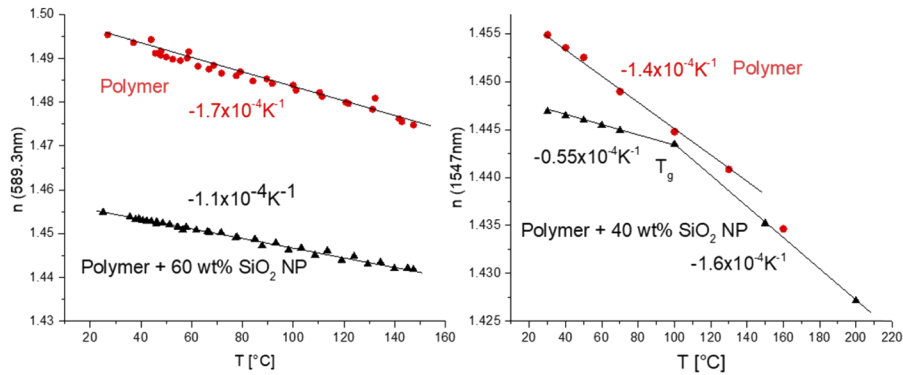


Fig. 4. Temperature dependencies of refractive index (numbers – TOCs) for direct introduction of NPs into polymer matrix (red circles correspond to unfilled polymer, black triangles to nanocomposite): left – ellipsometry (Polymer 2); right - m-line spectroscopy (Polymer 1).

3.2. Incorporation of NPs into the polymer side chain

As the next approach, we tried to incorporate NPs into polymer side chain. For that aim, we attempted to use NPs modified by monomer in the co-polymerization. The NPs S125 and DP5820 from Nyacol, NPs from IOLITEC modified with methacrylate and double bond, and porous NPs from IOLITEC, which were modified by 3-(trimethoxysilyl)propyl methacrylate to introduce methacrylate functionality, were applied in this case. Trifluoroethyl methacrylate (alternatively pentafluorostyrene) and glycidyl methacrylate were used as co-monomers. The incorporation of NPs into material was proved by TGA (20-30 wt.% of SiO_2 -residue). In most of these cases, the co-polymers could be obtained, but they exhibited low solubility in solvents suitable for film preparation. Therefore, the film thickness was only sufficient for thermo-optical measurements, but not for propagation loss measurement. Thicker films could be obtained using casting instead of spin-coating, but the quality of casted films was not sufficient for propagation loss measurement (uneven thickness). A tentative explanation of copolymer low solubility is partial interchain reaction between double bond moieties of different polymer chains (cross-linking). It seems plausible explanation as the concentration of localized double bonds on the NP surface could be high. The results of thermo-optic measurements for such polymers are collated in Table 4.

Table 4. Thermo-optic data for NP-containing copolymers.

Copolymer with	Ellipsometry		m-line spectroscopy	
	TOC [10^{-4} K^{-1}]	T_g [$^{\circ}\text{C}$]	TOC [10^{-4} K^{-1}]	T_g [$^{\circ}\text{C}$]
Modified DP5820	−1.65	100		
IOLITEC methacrylate modified	−1.7	not detected	−1.2	not detected
Modified porous from IOLITEC	−1.2	not detected	−1.1	not detected
IOLITEC double bond modified	−1.55	not detected	−1.3	not detected
IOLITEC methacrylate modified, copolymer with PFS			−(0.9-1.3)	not detected

The examples of ellipsometric and m-line measurements are presented in Fig. 5.

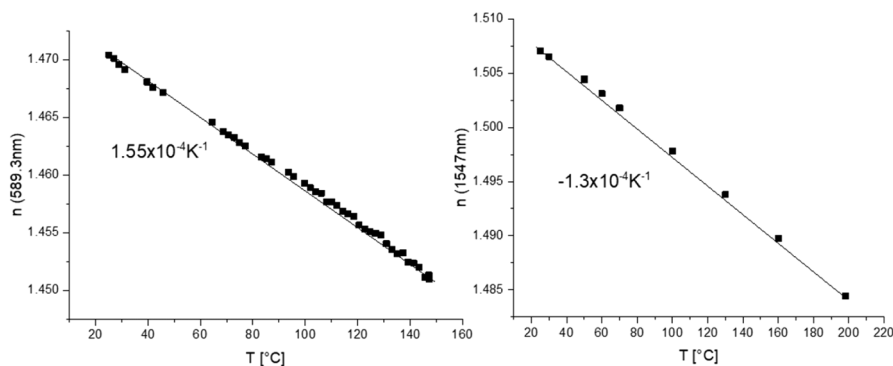


Fig. 5. Temperature dependence of refractive index (TOCs of corresponding materials are shown) for polymer incorporating SiO_2 NPs in side chain using IOLITEC double bond modified SiO_2 NPs: left – ellipsometry; right - m-line spectroscopy.

It seems that there is no clear trend in this case while the values of TOC are on the level of basic fluorinated polymers and direct comparison is not possible. The only impact we can find in this case is the distinctive suppression of glass transition, which was not detected in the measured temperature range, while similar polymers without NPs show T_g of *ca.* 100-120 $^{\circ}\text{C}$. This could be the influence of NPs introduction into polymer chain.

3.3. *In situ* formation of SiO_2 NPs

As the last approach, we have tried to incorporate silica NPs *in situ* (see Fig. 3). Siloxane-containing co-monomer was used in this case for the copolymerization with trifluoroethyl methacrylate (or pentafluorostyrene) and glycidyl methacrylate. By cross-linking of the polymer chains in the layer under influence of UV light in the presence of photoacid generator (followed by annealing) two reactions take place [17]. In addition to opening of the oxirane rings as it is exhibited in general reaction (Fig. 2), in the presence of water vapors from air the photoacid catalyzes the sol-gel reaction of siloxane groups that finally leads during annealing (evaporation of ethanol and water) to the formation of silica-like structures. Unfortunately, this approach has its disadvantages, namely, copolymer could not be separated and has to be used directly from the reaction solution. In addition, the solution of copolymer exhibits a short lifetime (*ca.* 1 month) and finally it is gelled due to proceeding of sol-gel reaction. While ellipsometric measurement exhibited TOC of *ca.* $-1.25 \times 10^{-4} \text{ K}^{-1}$ (steep fall of refractive index at the beginning could be

attributed to the loss of residual water), m-line measurement yielded $-(0.95\text{--}1.15)\times 10^{-4} \text{ K}^{-1}$ (Fig. 6).

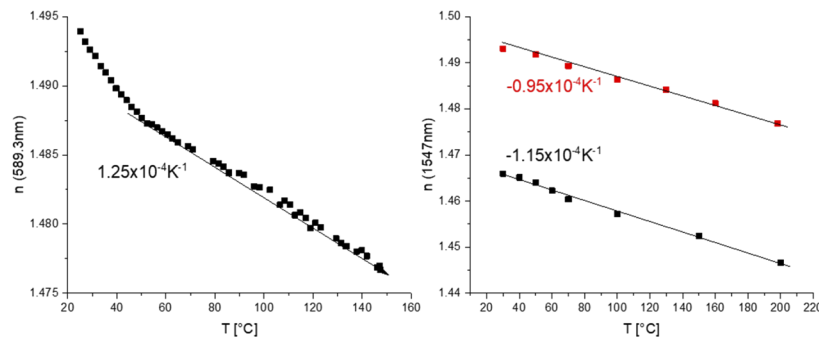


Fig. 6. Temperature dependence of refractive index (TOCs of corresponding materials are shown) for polymer with SiO₂ NPs obtained by *in situ* sol-gel reaction: left – ellipsometry; right – m-line spectroscopy.

Since in this case polymer can be fabricated only with silica NPs inside, it is not clear whether the formation of these NPs *in situ* influences TOC. However, the glass transition of the polymer could not be observed up to a temperature of 200 °C. An additional cross-linking *via* Si–O–Si by the formation of silica *in situ* could be responsible for this effect.

3.4. Optical propagation losses

It is clear that NPs could affect thermo-optical properties of polymers reducing as expected TOC and suppressing glass transition. More interesting question is how NPs could affect optical propagation losses. The level of optical losses is rather important for practical application in planar waveguide. As already stated, it was possible to obtain layers of more than 5 μm thickness and consequently attempt to measure optical losses only for nanocomposite samples obtained by direct introduction of silica NPs. Another problem was the refractive index of the layers after introduction of NPs. As optical losses are measured on fused silica substrate, which have a refractive index of 1.444 at 1550 nm, the refractive index of a planar polymer waveguide layer has to be at least 1.45 or higher to enable waveguiding mode. Therefore, it was not possible to use the co-polymer with participation of fluorinated acrylate due to their too low refractive index. Instead, the co-polymers with halogenated aromatic components (as core material) have to be used (Fig. 2). The last co-polymers have a tendency to be brittle and in combination with the fact that NPs in high concentration also increase this trend, we had a processability problem. However, by selection of copolymer composition (see Table 2), by using moderate NP concentrations (up to 30 wt%), and by gentle removing of the excess of low boiling solvents, we were able to obtain planar waveguiding layers with the nanocomposites. Thus, all samples for optical loss measurements were obtained using MEK-ST NPs from Nissan and different copolymers according to Scheme (Fig. 2), containing either chlorinated monomer or low concentration of fluorinated monomer to achieve refractive index of final nanocomposite higher than 1.45 (1547nm). The examples of measurements and the results of optical loss measurements for such pair combinations are demonstrated in Figs. 7 and 8.

It seems that the optical losses in nanocomposite waveguides are comparable with starting polymers (Fig. 7). In addition, it is clear from the best measurements that introduction of NPs into waveguide polymer layer actually did not influence propagation losses significantly (Fig. 8). The level of optical losses is rather important for practical application in planar waveguide and the target value for the fabrication of optical microchip is to keep losses below 0.6 dB/cm [29]. Therefore, the results presented in Fig. 8 demonstrate that by using small NPs (in this case NPs

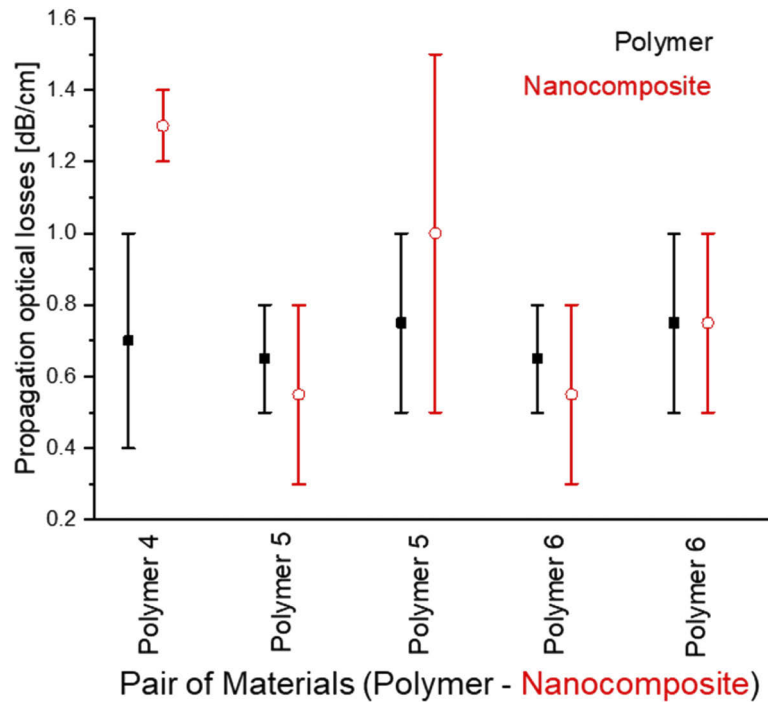


Fig. 7. Comparison of optical propagation losses between polymer and polymer composites with SiO₂ NPs from several experiments (each experiment corresponds to a pair of materials, one of them is polymer (black, full squares, polymer composition is in Table 2) and another is nanocomposite based on the same polymer (red, empty circles)). Value spreading corresponds to the measurements using different samples of the same material and measurements along different optical passes on the same sample.

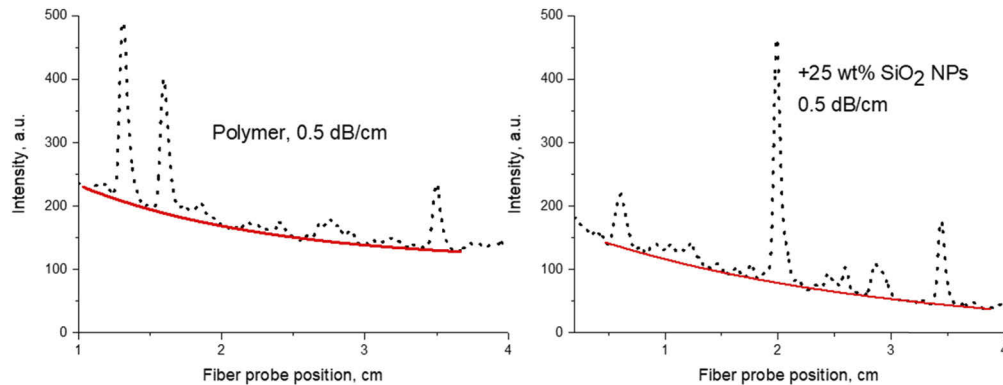


Fig. 8. Examples of propagation losses measurements for Polymer 4 and its nanocomposite with SiO₂ NPs (red line is exponential fit): left – unfilled polymer, right - nanocomposite.

MEK-ST from Nissan of 15-20 nm in diameter) it is possible to achieve such values of optical losses.

Higher optical losses for nanocomposites in some experiments can be tentatively explained by the difficulty of building of comparatively thick layer of nanocomposites of good optical quality due to trend of cracks formation compared with polymer layers without NPs (insufficient processability,

Fig. 9). The formation of pattern was also observed in some cases for nanocomposites layers. Hence, films building properties require further improvement.

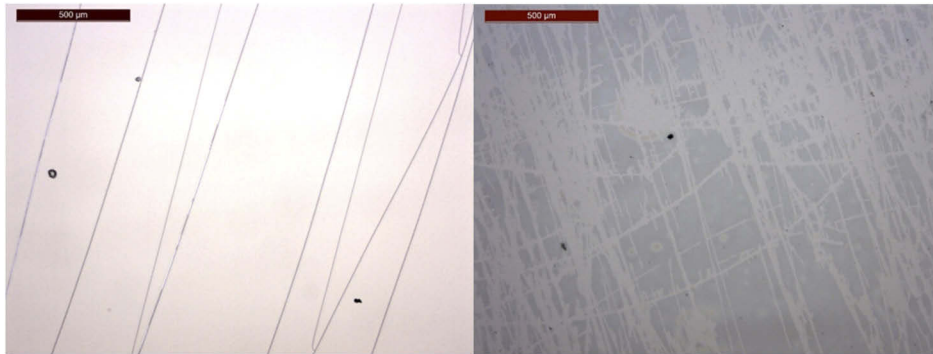


Fig. 9. Examples of defects (cracks) on the surface of the nanocomposite films: left – sample on the fused silica substrate for optical loss measurement (optical loss 1.2–1.4 dB/cm), nanocomposite with 30 wt% of SiO₂ NPs from MEK-ST; right – film on Si wafer substrate, nanocomposite with 50 wt% of SiO₂ NPs from MEK-ST.

It means that this approach is promising and further work will be required where by better choice of NPs and polymer matrix improved materials can be obtained.

4. Conclusions

Successful fabrication of nanocomposites by the direct introduction of Nissan SiO₂ NPs into polymer matrix has been demonstrated. The nanocomposites films possess almost the same propagation losses in planar waveguide scheme as these of unfilled polymer, having significantly lower thermo-optic coefficient. Other methods of SiO₂ NP introduction (as in a polymer side chain and *in situ* SiO₂ formation) were less successful, but such nanocomposites exhibited higher glass transition temperatures.

Funding

Open Access Publication Funds of the Technische Hochschule Wildau – Technical University of Applied Sciences; Deutsche Forschungsgemeinschaft; Bundesministerium für Bildung und Forschung (03VKCT1C).

Acknowledgement

The work was financially supported by German Federal Ministry of Education and Research (Project PolyPhotonics, Support Code 03VKCT1C). We acknowledge support by the German Research Foundation and the Open Access Publication Funds of the Technische Hochschule Wildau – Technical University of Applied Sciences Wildau.

Disclosures

The authors declare that there are no conflicts of interest related to this article.

References

1. R. Yoshimura, M. Hikoto, S. Tomaru, and S. Imamura, “Low-loss polymeric optical waveguides fabricated with deuterated polyfluoromethacrylate,” *J. Lightwave Technol.* **16**(6), 1030–1037 (1998).

2. T. Matsuura, S. Ando, S. Sasaki, and F. Yamamoto, "Polyimides derived from 2,2'-Bis(trifluoromethyl)-4,4'-diaminobiphenyl. 4. optical properties of fluorinated polyimides for optoelectronic components," *Macromolecules* **27**(22), 6665–6670 (1994).
3. H. J. Lee, M. H. Lee, M. C. Oh, J. H. Ahn, and S. G. Han, "Crosslinkable polymers for optical waveguide devices. II. Fluorinated ether ketone oligomers bearing ethynyl group at the chain end," *J. Polym. Sci., Part A: Polym. Chem.* **37**(14), 2355–2361 (1999).
4. J. W. Kang, J. P. Kim, W. Y. Lee, J. S. Kim, J. S. Lee, and J. J. Kim, "Low-loss fluorinated poly(arylene ether sulfide) waveguides with high thermal stability," *J. Lightwave Technol.* **19**(6), 872–875 (2001).
5. G. Fischbeck, R. Moosburger, C. Kostzewa, A. Aeben, and K. Petermann, "Singlemode optical waveguides using a high temperature stable polymer with low losses in the 1.55 μm range," *Electron. Lett.* **33**(6), 518 (1997).
6. M.-C. Oh, K.-J. Kim, W.-S. Chu, J.-W. Kim, J.-K. Seo, Y.-O. Noh, and H.-J. Lee, "Integrated photonic devices incorporating low-loss fluorinated polymer materials," *Polymers* **3**(3), 975–997 (2011).
7. C. Dreyer, J. Schneider, K. Göcks, B. Beuster, M. Bauer, N. Keil, H. Yao, and C. Zawadzki, "New reactive polymeric systems for use as waveguide materials in integrated optics," *Macromol. Symp.* **199**(1), 307–320 (2003).
8. O. Ziemann, J. Krauser, P. E. Zamzow, and W. Daum, *Optical Short Range Transmission Systems* (Springer-Verlag Berlin Heidelberg, 2008), 901 pp.
9. T. Ishigure, S. Yoshida, K. Yasuhara, and D. Suganuma, "Low-loss single-mode polymer optical waveguide at 1550-nm wavelength compatible with silicon photonics," *IEEE Electronic Components & Technology Conference*, 768 (2015).
10. J. Noack, C. Fritz, C. Flügel, F. Hemmann, H.-J. Gläsel, O. Kahle, C. Dreyer, M. Bauer, and E. Kemnitz, "Metal fluoride-based transparent nanocomposites with low refractive indices," *Dalton Trans.* **42**(16), 5706 (2013).
11. J. Noack, L. Schmidt, H.-J. Gläsel, M. Bauer, and E. Kemnitz, "Inorganic-organic nanocomposites based on sol-gel derived magnesium fluoride," *Nanoscale* **3**(11), 4774 (2011).
12. C.-C. Chang and W.-C. Cheng, "Synthesis and optical properties of polyimide-silica hybrid thin films," *Chem. Mater.* **14**(10), 4242–4248 (2002).
13. M. Signoretto, I. Suárez, V. S. Chirvony, R. Abargues, P. J. Rodríguez-Cantó, and J. Martínez-Pastor, "Polymer waveguide couplers based on metal nanoparticle-polymer nanocomposites," *Nanotechnology* **26**(47), 475201 (2015).
14. H. Zou, S. Wu, and J. Shen, "Polymer/silica nanocomposites: preparation, characterization, properties, and applications," *Chem. Rev.* **108**(9), 3893–3957 (2008).
15. C. Pitois, S. Vukmirovich, A. Hult, D. Wiesmann, and M. Robertson, "Low-loss passive optical waveguides based on photosensitive poly(pentafluorostyrene-co-glycidyl methacrylate)," *Macromolecules* **32**(9), 2903–2909 (1999).
16. N. Nourschagh, E. M. Starr, N. I. Fox, and S. G. Jones, "Simple technique for measuring attenuation of integrated optical waveguide," *Electron. Lett.* **21**(18), 818 (1985).
17. V. Prajzler, P. Nekvindova, P. Hyps, and V. Jerabek, "Properties of the optical planar polymer waveguides deposited on printed circuit boards," *Opt. Commun.* **24**, 442–448 (2015).
18. V. Prajzler, P. Hyps, R. Mastera, and P. Nekvindova, "Properties of siloxane based optical waveguides deposited on transparent paper and foil," *Opt. Commun.* **25**, 230–235 (2016).
19. V. Prajzler, M. Neruda, and P. Nekvindova, "Flexible multimode polydimethyl-diphenylsiloxane optical planar waveguides," *J. Mater. Sci.: Mater. Electron.* **29**(7), 5878–5884 (2018).
20. O. Kahle, U. Wielsch, H. Metzner, J. Bauer, C. Uhlig, and C. Zawadzki, "Glass transition temperature and thermal expansion behaviour of polymer films investigated by variable temperature spectroscopic ellipsometry," *Thin Solid Films* **313-314**, 803–807 (1998).
21. A. Chemtob, D.-L. Versace, C. Belon, C. Croutxé-Barghorn, and S. Rigolet, "Concomitant organic- inorganic UV-curing catalyzed by photoacids," *Macromolecules* **41**(20), 7390–7398 (2008).
22. H. Gao, D. Yorifuji, Z. Jiang, and S. Ando, "Thermal and optical properties of hyperbranched fluorinated polyimide/mesoporous SiO_2 nanocomposites exhibiting high transparency and reduced thermo-optical coefficients," *Polymer* **55**(12), 2848–2855 (2014).
23. Y. Q. Rao and T. N. Blanton, "Polymer nanocomposites with a low thermal expansion coefficient," *Macromolecules* **41**(3), 935–941 (2008).
24. M. Enhessari, K. Ozaee, E. Karamali, and M. R. Ahmadi, "Fabrication and Thermal Properties of Polyimide/Ba_{0.77}Sr_{0.23}TiO₃ Nanocomposites," *Int. J. Polym. Mater.* **61**(2), 89–98 (2012).
25. X. W. Shi, H. Lian, X. S. Yan, R. Qi, N. Yao, and T. Li, "Fabrication and properties of polyimide composites filled with zirconium tungsten phosphate of negative thermal expansion," *Mater. Chem. Phys.* **179**, 72–79 (2016).
26. J. González-Benito, E. Castillo, and J. F. Caldito, "Coefficient of thermal expansion of TiO₂ filled EVA based nanocomposites. A new insight about the influence of filler particle size in composites," *Eur. Polym. J.* **49**(7), 1747–1752 (2013).
27. R. Voo, M. Mariattia, L. C. Sim, and Polym, "Thermal properties and moisture absorption of nanofillers-filled epoxy composite thin film for electronic application," *Polym. Adv. Technol.* **23**(12), 1620–1627 (2012).
28. S. I. Ahn, S. W. Ohk, J. H. Kim, and W.-C. Zin, "Glass transition temperature of polymer nanocomposites: prediction from the continuous-multilayer mode," *J. Polym. Sci., Part B: Polym. Phys.* **47**(22), 2281–2287 (2009).
29. C. Zawadzki and M. Schirmer, "Der wellenleiter-chip - photonische bauelemente aus polymeren," *Photonik* **1**, 43 (2018).