High-performance polymeric materials for waveguide applications

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ABSTRACT

The ever-increasing need for economical, reliable, and high-performance optical interconnects for telecommunication and data communication markets demands new innovative solutions. Polymer technology being developed at BFGoodrich is focused on satisfying this demand. It is based on proprietary polynorbornene polymers that exhibit excellent optical, thermal and mechanical properties essential for fabrication of reliable components for integrated optics. Typical polymer waveguide systems exhibit a tradeoff between thermal and optical performance. The uniqueness of the polynorbornene system is that these tradeoffs are minimized. The intrinsic properties of the polynorbornene system include low transmission loss (<0.1 dB/cm at 820 nm), wide spectral range (<0.4 dB/cm at 450 nm and <0.1 dB/cm at 515-870 nm), low birefringence (Δn (in plane) $<10^{-5}$, Δn (out of plane) $<10^{-3}$ at 820 nm), consistent difference in index over a wide temperature range, long-term thermal stability (>2000 hours at 125 ºC), high glass transition temperature (>280 °C), and low moisture absorption (<0.1%). The combination of these characteristics offers advantages over existing plastic materials for visible and near IR applications such as those used in the datacom market. Candidate materials have been identified as core and cladding components for optical waveguides. The refractive index of a typical core material is 1.53, and of a typical clad material, 1.50 at 820 nm. The difference in index between core and cladding is ~0.03 over a broad range of wavelength (515-870 nm). Preliminary results indicate that the difference in index between core and cladding tracks with temperature, which is in line with our expectation since these polymers have similar structures at the molecular level. Fabrication of functional waveguides has been demonstrated using a conventional cast and cure process at the lab scale. Optical performance of the constituent materials and the waveguide devices will be discussed in the paper.

Keywords: polymers, polynorbornene, optical waveguide, low loss, spectral range, birefringence, thermal stability, glass transition temperature, moisture absorption, difference in index *vs.* temperature.

1. INTRODUCTION

The demand for continuous increase in transmission speed, data capacity and data density in integrated optical and optoelectronic circuits drives innovations in areas of broadband communications, high-capacity information storage, and large screen and portable information display. Although glass optical fibers are routinely used for high-speed data transfer over long distances, they are inconvenient for complex high-density circuitry because of their high density, poor durability and high cost of fabrication for complex photonic circuits. Polymeric materials hold great promise for constructing cost effective, reliable, passive and active integrated components capable of performing the required functions for integrated optics. Many laboratories worldwide have done extensive research in investigating new functions for existing polymers as well as engineering improved optical polymers. Many of polymers, such as polyacrylates,[1-4] polyimides[5-7] and others,[8,9] show promise in generating, processing, transmitting, detecting, and storing light signals.

BFGoodrich has over three decades of experience with cyclic olefins (e.g., norbornene-type monomers) and polymers derived therefrom. Recently, we have developed a novel catalyst system[10] based on Group VIII transition metals that allows the addition polymerization of norbornene-type monomers.[11] The innovation of the catalyst system leads to a new generation of polycyclic olefins, enabling cyclic olefin based waveguide polymers, with intrinsically good optical, mechanical and moisture absorption properties. We are currently working with our partners at 3M Company towards the development of an optical waveguide system (both core and cladding) and optical TAB (tape automated bonding) materials for on-board, high-speed data links. This partnership has been supported by an Advanced Technology Program grant from the National Institute of Standards and Technology. For this new class of optical polymers, we have demonstrated their intrinsic properties, fabrication of optical waveguides at lab scale, and optical performance of the waveguides. With help

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from many of our customers, we are currently developing technologies that enable mass production of optical waveguides, and in the meantime, BFGoodrich is moving toward commercializing these optical materials.

2. MATERIALS

The new catalyst system enables us to polymerize norbornenes having different functional side groups. We have developed a class of polymers that have low moisture absorption, high glass transition temperature (Tg), low transmission loss, low birefringence, and consistent difference in index over a wide range of temperature. In addition, we have the capability of using different monomers to tailor both the optical and mechanical properties of our polymers to meet the requirements of various applications. Currently, we are targeting three different areas: plastic substrates for the flat panel display (400-700 nm) market, optical waveguides for the datacom (820 nm) market, and optical materials for the telecom (1550 nm) market. In this paper, we will limit our discussion to the area of datacom applications; our focus is on the materials, fabrication and performance of optical waveguides.

2.1. General Description of BFGoodrich Waveguide Polymers

Our products for datacom applications come as two-part (components A and B) solvent-less liquid. Both components consist of norbornene-type monomers and anti-oxidant (AO). Component A also contains a procatalyst and component B contains a cocatalyst. Mixing components A and B in a 1/1 ratio generates the active polymerization catalyst *in situ*. The mixture is heated to advance the polymerization. This is evident from an increase in viscosity, which can be controlled in a fabrication process by adjusting curing temperature and time. A variety of optical components, such as films, rods, blocks and those patterned with designed features, can be obtained by casting on appropriate molds. The type and concentrations of monomers, AO packages, catalyst and co-catalyst have been carefully chosen to achieve the desired optical, thermal, and mechanical properties.

Performance of this set of waveguide polymers is summarized in Table 1. Key material tests and characterizations are discussed as follows.

Table 1 Performance of BFGoodrich's waveguide polymers *vs.* desirable polymer attributes for multi-mode waveguide.

Key Attributes	BFG Waveguide Polymers
Refractive index: Δn(core-clad) ≥ 0.01	~0.03
Δn consistent with temperature	Demonstrated
Birefringence: low	In plane: $\Delta n \sim 10^{-5}$; out-of-plane: $\Delta n \sim 10^{-3}$
Optical loss: low material loss	<0.1 dB/cm 515-870 nm (<0.02 dB/cm at 820 nm)
low loss of waveguide	0.14 dB/cm
Oxidative stability: 2000 hours at 125 ºC in air	Demonstrated with several AO packages
Solder reflow compatible: T_g>250 ºC	T_g>280 ºC
Moisture absorption: low	<0.1%
Mechanically robust	Elongation ~ 20%

2.2. Intrinsic Optical Loss of Core and Cladding Materials

Intrinsic transmission loss of our materials was measured on polymer rods where fabrication imperfections are easily avoidable. Both core and cladding materials were fabricated into rods, 7 mm in diameter, and ~60 mm in length. The ends of the rods were carefully polished. Loss measurements were performed on these rods using the cleave-back method. Intrinsic transmission loss of both core and cladding materials was measured between 400 and 1100 nm, and the results are shown in Fig. 1. The solid line in Fig. 1 represents the transmission loss of the core material, and the dashed line, the loss of the cladding material. Both core and cladding materials exhibit similar loss values, <0.1 dB/cm in the wavelength range of 515-870 nm. At 820 nm, the core and cladding materials exhibit loss values of <0.02 dB/cm (Fig. 1b).

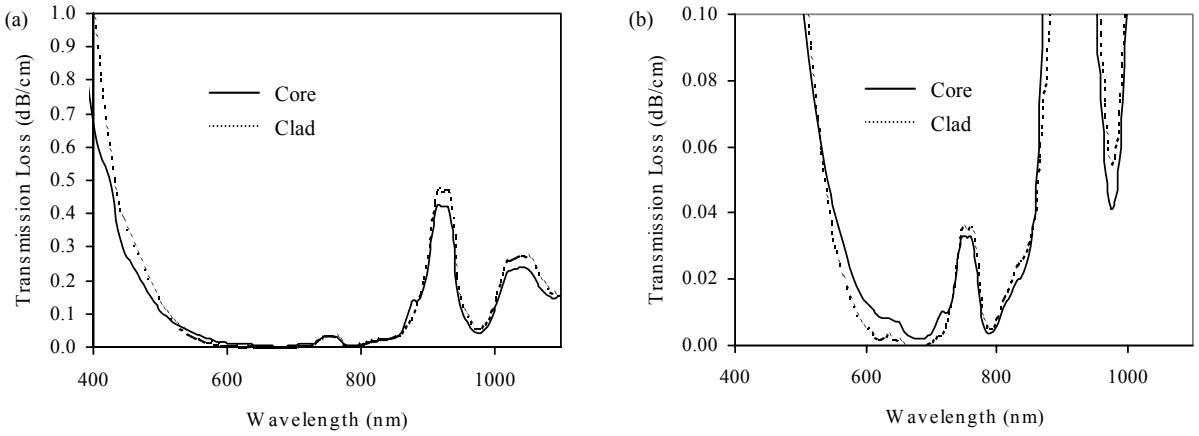

Fig. 1 Transmission loss of polymer rods of the core and cladding materials as a function of wavelength. Plot (b) is an expansion of plot (a) in the range of transmission loss of 0-0.1 dB/cm.

2.3. Thermal Stability

A key limitation of organic materials in practical applications is their thermo-oxidative instability. Polymers are susceptible to thermo-oxidative degradation that may affect desired optical and mechanical properties. For integration of polymeric optical components into mainstream electronic applications, they must meet the rigorous thermal requirements already being demanded in the electronics industry.

2.3.1. High-temperature stability of polymer films in air

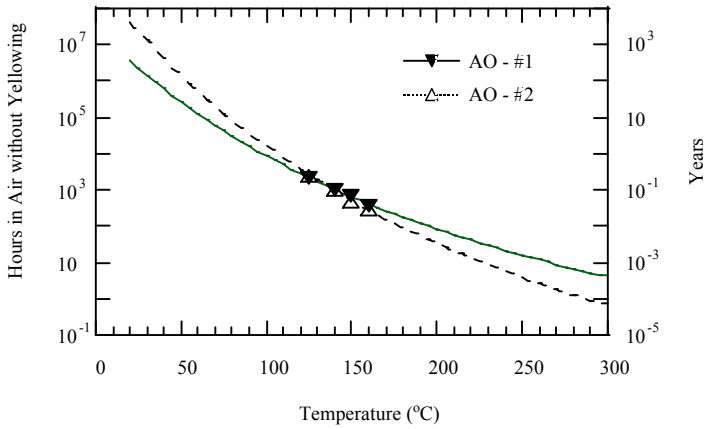

Fig. 2 Arrhenius extrapolation of lifetime in air of the core material with two different AO packages.

To meet the thermal stability requirements for different applications (which correspond to lifetime of the devices at different operating temperatures), we have investigated a variety of AO packages and their compatibility with our core and cladding system. AO packages were carefully selected to maintain both mechanical and optical properties of the core and cladding materials. In fact, all the results shown in this paper were obtained on BFG waveguide materials containing preferred AO packages.

To determine the high-temperature stability of our waveguide materials, the tests were done on 150-μm thick free-standing films of the core and cladding compositions at 125º, 140º, 150º, and 160 °C in air. A failure point was determined to be the first sign of visual yellowing. The relationship of coloration and temperature were found to fit into the Arrhenius expression:

$$\log t = A + E_a/[R(T+273)],$$

where t is the time of exposure (in hours) to reach an extent of degradation, A is a constant, E_a is the activation energy for the chemical degradation process, R is the universal gas constant, and T is the temperature (in degrees Celsius) at which this degradation process occurs. We have found out that the core and cladding materials have similar thermo-oxidative stability. Figure 2 shows the measured failure points, at 125º, 140º, 150º, and 160 °C, of the core composition having two representative AO packages (AO #1 and AO #2). Also shown are the fits to the Arrhenius law. The two curves cross over at 135 ºC, which indicates that the combination of the core polymer with AO #1 performs better (gives longer lifetime) at higher (>135 ºC) operating temperatures and the combination with AO #2 does better at lower (<135 ºC) operating temperatures. Predicted stability at several temperatures of interest is listed in Table 2.

Table 2 Predicted stability of the core composition containing AO#1 and AO#2 at different temperatures.

Temperature (ºC)	AO #1	AO #2
25	>250 yr	>2500 yr
70	7 yr	22 yr
100	1 yr	2 yr
125	2200 h	2500 h
200	80 h	35 h
250	16 h	4 h

2.3.2. Optical loss at 820 nm as a function of aging

A much more relevant test with regard to practical applications, however, is the change in optical transmission loss as a function of thermal aging. Observed yellowing (coloration in the visible region) does not necessarily translate into increased transmission loss at the datacom wavelength (820 nm). To investigate the changes of intrinsic optical loss of both core and cladding materials on thermal aging, polymer rods were fabricated using AO#1, one of the preferred AO packages, and transmission loss at 820 nm was monitored as a function of time at 125 °C in air. Again, the values of transmission loss were measured using the cleave-back method. The results are plotted in Fig. 3. The transmission loss data conclusively indicates that the AO package #1 imparts excellent thermal stability to both the core and clad compositions. For a period of up to 2600 h at 125 ºC in air, the transmission loss value of the core composition remained less than 0.1 dB/cm. The corresponding time at 125 °C in air for the cladding composition was about 3400 h.

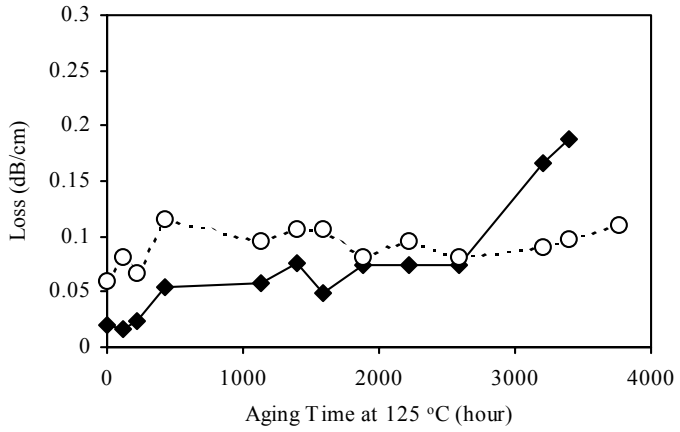

Fig. 3 Intrinsic transmission loss of the core (◆) and cladding (O) materials as a function of time at 125 °C in air.

2.4. Temperature Dependence of Refractive Index

Performance of many optical systems relies on having a consistent difference in refractive index between core and cladding materials in the temperature range of interest. We have designed both core and cladding materials to have similar molecular structures, so that the difference in refractive index tracks with temperature. To demonstrate this, we measured the

refractive indices of both core and cladding materials (with AO #1), in the form of a polymer film, using an Abbe refractometer. The results are shown in Fig. 4. The difference in indices for the core and cladding materials is consistent (~0.03 at 589 nm) in the temperature range of 10-68 ºC (controlled by a water bath). The difference in values of *dn/dt* between the core (248 ppm/ºC) and cladding (245 ppm/ºC) materials is within our experimental error.

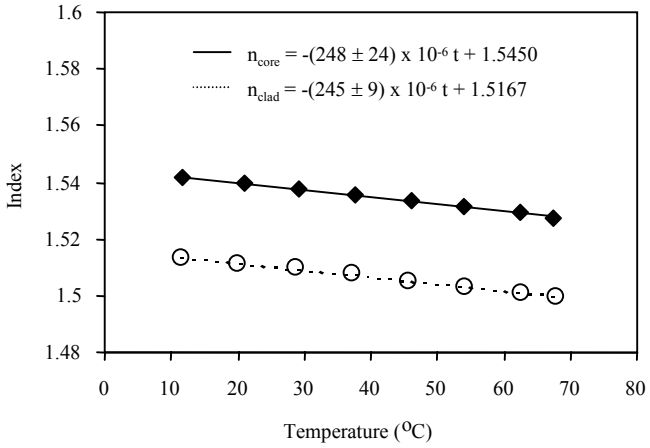

Fig. 4 Changes of refractive indices (at 589 nm) of the core (◆) and cladding (O) materials as a function of temperature.

2.5. Refractive Index Dispersion

A key characteristic for practical applications is material dispersion. To obtain a general idea of the refractive index dispersion of our core and cladding materials, we fabricated sheets of films and measured the refractive indices for both the core and cladding materials at 589 nm, 633 nm and 820 nm at 20 °C. Figure 5 shows the measured values of index and Cauchy fits for both the core and cladding materials in the wavelength range of 515-870 nm. The difference in refractive index between the core and cladding is consistent and determined to be ~0.03 within this wavelength range.

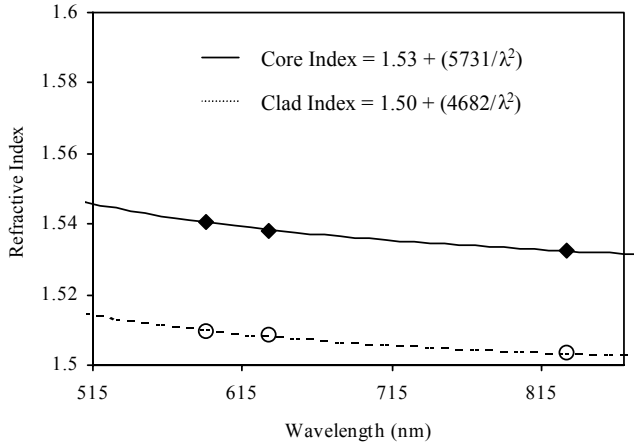

Fig.5 Refractive indices of the core (◆) and cladding (O) materials measured at 589 nm, 633 nm, and 830 nm, and Cauchy fits of the core (solid line) and cladding (dotted line) calculated based on these data points.

3. FABRICATION OF WAVEGUIDES

Many methods have been used to fabricate polymeric waveguides: examples include micromolding/embossing,[12] reactive ion etching,[13,14] UV laser[15] and e-beam[16] writing, photochemical delineation,[17] photo-bleaching,[18] induced dopant

diffusion (photo-induced dopant diffusion,[19] photolocking[20] and selective polymerization[21]), selective poling of electro-optically active molecules induced by an electric field,[22] and polymerization of self-assembled prepolymers.[23] These techniques produce optical waveguides with accuracy in the micron or even sub-micron range. However, production costs for large volumes are too high in most cases. Hence, conventional molding techniques like injection or compression molding have been modified to perform large-volume fabrication of polymeric microcomponents.[12,24,25] Although other techniques such as reactive ion etching and excimer laser ablation were demonstrated to effectively etch our polynorbornene materials to desired shape and dimension, the core and cladding materials described in the preceding sections are designed to fit into more economical and continuous fabrication techniques. Fabrication of optical waveguides is achieved by conventional molding techniques and several proprietary modifications to the extant technologies.

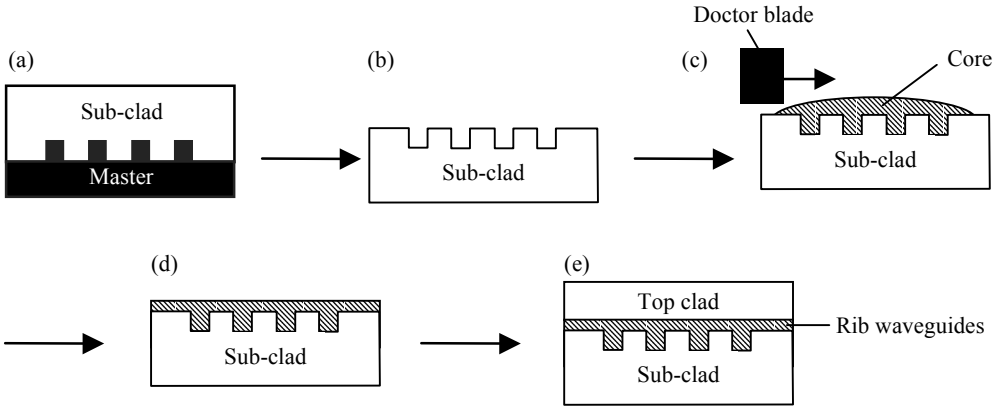

Fig. 6 Fabrication of rib waveguides using a conventional clad-first approach.

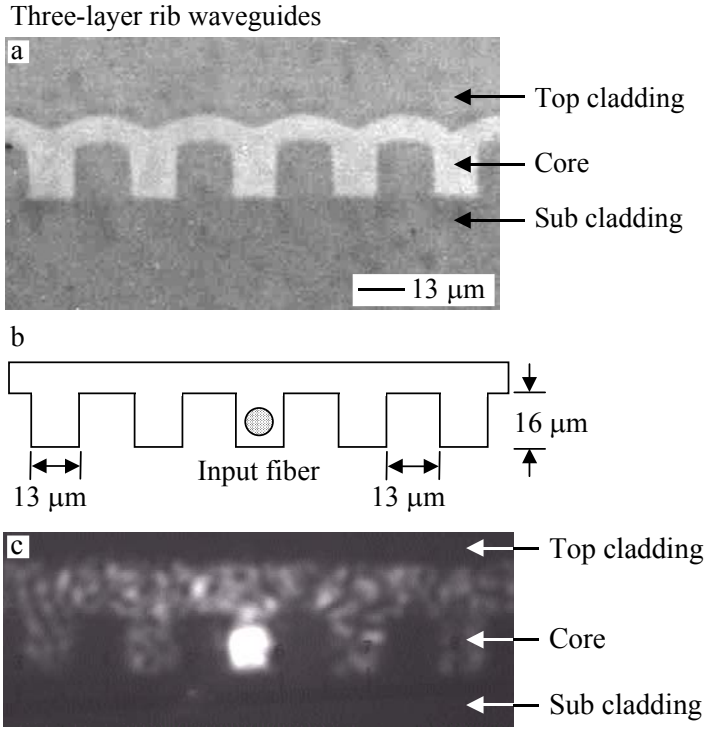

Fig. 7 (a) Optical micrograph of a cross section of three-layer rib waveguides made using a conventional clad-first approach. (b) Schematic diagram of the end view of a rib waveguide array (13 μm wide, 16 μm tall, spaced by 13 μm) with the position of an input optical fiber shown as a shaded circle. (c) Photograph of the waveguide output when light from a diode laser (λ = 820 nm) was coupled into the central waveguide as shown in (b).

3.1. Conventional Clad-First Molding Technique

Most conventional molding processes of fabrication of waveguides are done in a clad-first fashion.[12] For example, in a generic process (Fig. 6) of making waveguides, a cladding film is formed by casting against a master in a molding process such as injection molding, hot embossing and reactive casting (Fig. 6a-b). A liquid core material is then applied onto the featured side of the cladding film (Fig. 6c) and forced into the grooves by pressure. Curing of the core material results in a two-layer film containing waveguides (Fig. 6d-e). Our early attempt of making waveguides using this conventional clad-first approach yielded arrays of buried rib waveguides as shown in Fig. 7a. A careful balance[26] of the dimensions (height, width, spacing, and thickness of the slab region) of the rib guides along with control over the difference in index and operating wavelength can lead to a waveguide structure in which light is well confined (Fig. 7b).

3.2. Core-First Molding Approach

An alternative to the clad-first approach is the core-first approach. Compared with the conventional clad-first approach, the fabrication steps in the core-first approach were executed in a reversed order, which are illustrated in Fig. 8. A general process is described as follows. A mixture of the core material was poured onto the surface of a master (e.g., Ni, Si masters, etc.) having grooves of the desired waveguide core dimensions (Fig. 8a-b). A doctor blade was set to rest directly on the surface of the master and used to scrape away the excess liquid core mixture (Fig. 8b-c). After the core material left in the grooves was fully cured (Fig. 8c), a mixture of the cladding material was poured onto the core-coated master and the thickness of the cladding layer was again controlled by a doctor blade (Fig. 8d). Upon curing under a proper condition, the polymer film containing a thick layer of cladding and isolated core structures was removed from the master and flipped over (Fig. 8e-f). A two-layer polymer film containing isolated channel waveguides on a continuous cladding film was obtained. A top cladding layer was then applied onto the core side of the film (Fig. 8g). Curing of this third layer resulted in a three-layer polymer film containing isolated channel waveguides buried between two cladding layers (Fig. 8h).

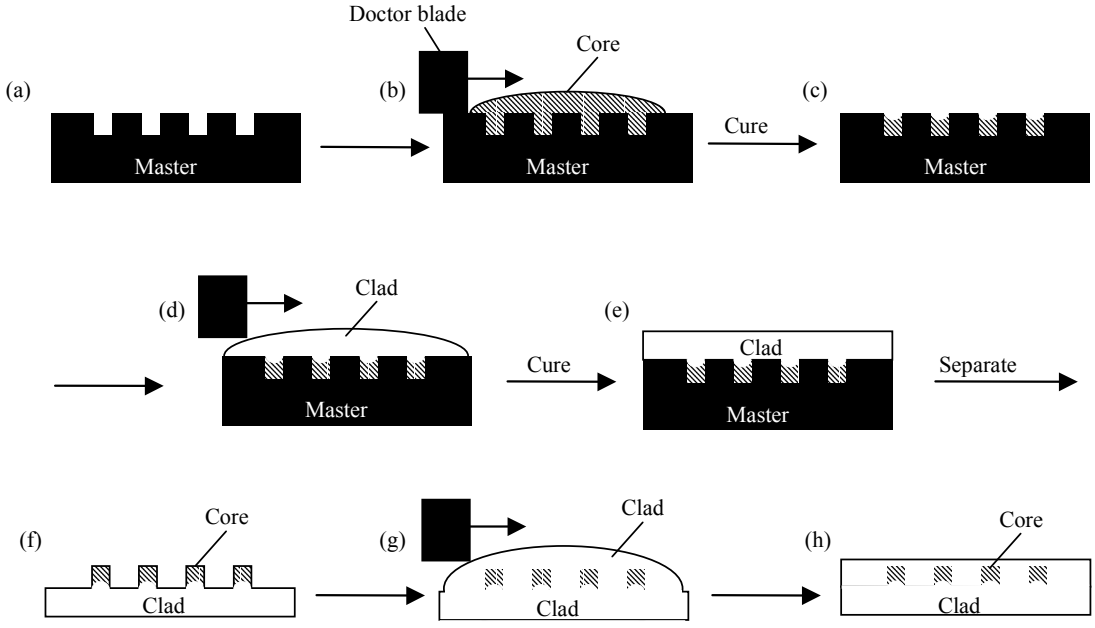

Fig. 8 Schematic diagram outlining the fabrication of buried channel waveguides using the core-first approach.

Compared with the clad-first approach, this core-first approach makes the core structures of waveguides by casting on a master (e.g., Ni or Si) that has no interaction with the liquid core precursor. This modification in the fabrication process allows the complete removal of the slab region of the core layer and also enables an easy filling of fine channels by using a low-viscosity core prepolymer mixture, which simplifies the production of isolated, buried channel waveguides. Optical

micrographs of representative samples, a two-layer and three-layer waveguide structures, are shown in Fig. 9a-b. Light was coupled into and confined in these waveguides. No cross coupling between waveguides was observed (Fig. 9d).

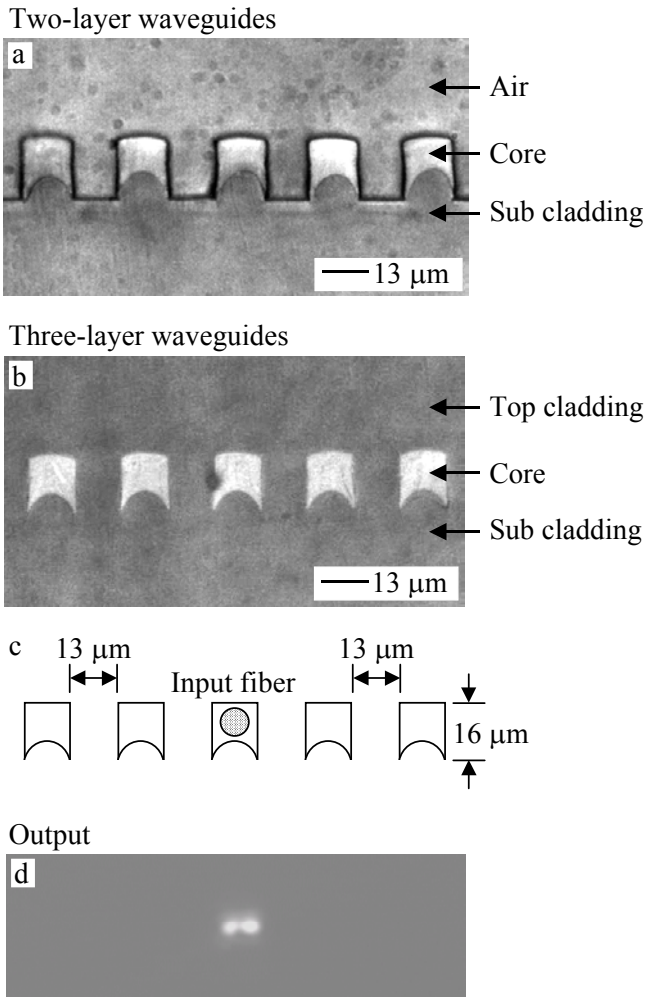

Fig. 9 (a-b) Optical micrographs of two-layer (a) and three-layer (b) buried channel waveguides fabricated using the core-first approach. (c) Schematic diagram of the end view of a waveguide array (13 μm wide, 16 μm tall, spaced by 13 μm) with the position of an input optical fiber shown as a shaded circle. (d) Photograph of the waveguide output when light from a diode laser (λ = 820 nm) was coupled into a single waveguide as shown in (c). The output pattern shows that the guide was multimode at 820 nm and there was no cross coupling between adjacent guides.

3.3. Other technology

We have also developed other waveguide fabrication techniques that have the potential of enabling mass production of straight, isolated buried channel waveguides on rolls of flexible film. Cross sections of test samples are shown in Fig. 10a and c. The length of the waveguides is ~11 inches, which is limited by the size of the hand-cast films (8 in x 11 in) used in the lab test. The waveguides shown in Fig. 10 are multimode waveguides at 820 nm. Light was coupled in an individual waveguide and confined in that guide (Fig. 10b and d). The transmission loss of the waveguide was measured, by the cleave-back method, to be 0.14 dB/cm at 820 nm, suggesting that the loss in waveguides came from both the intrinsic material loss (<0.1 dB/cm) and fabrication imperfections. Our study of the thermal stability of this kind (e.g. flat ribbon cable) of waveguide structures is still in progress. We anticipate that the thermal aging behavior of the core and cladding polymers in the form of waveguide is similar as those of bulk materials (films and rods), but this hypothesis is yet to be demonstrated experimentally.

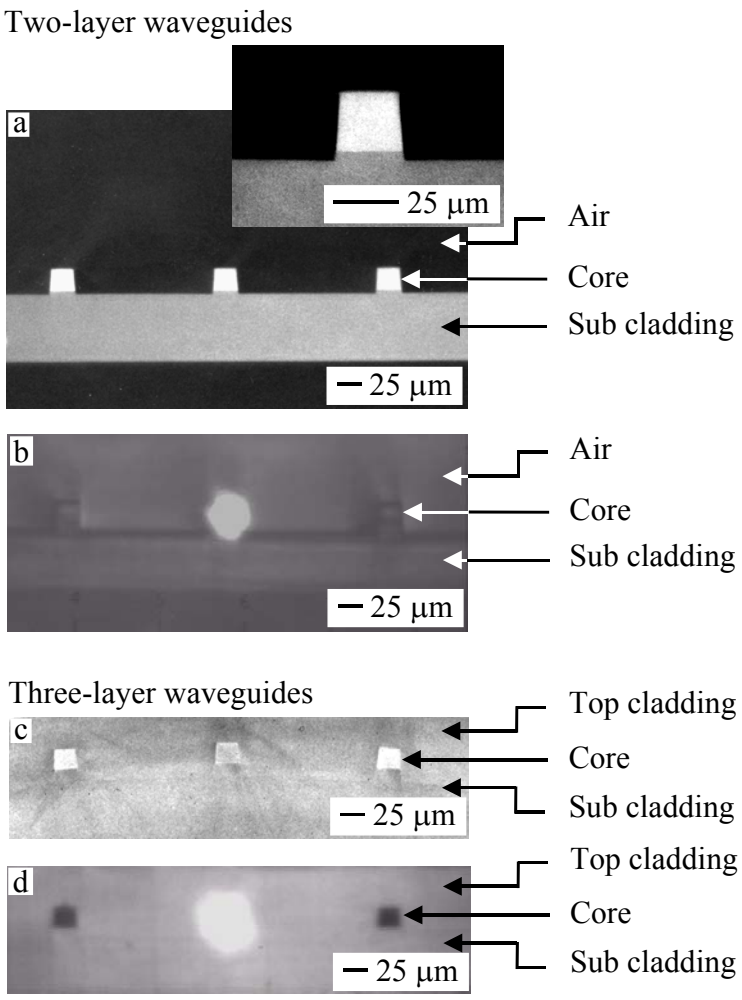

Fig. 10. Optical micrographs of two-layer (a) and three-layer (c) isolated channel waveguides fabricated using the technique discussed in section 3.3. Light from a diode laser (λ = 820 nm) was coupled into a single waveguide. (b) Photograph of the output of a two-layer waveguide shown in (a). (d) Photograph of the output of a three-layer waveguide shown in (c). In order to make the positions of individual guides visible in pictures b and d, a table lamp was used to illuminate the output ends of the waveguides. The intensity of the input light from a diode laser was maximized when the output pictures (b and d) were taken. These output patterns indicate that there was no cross coupling between adjacent guides.

4. CONCLUSIONS

BFGoodrich has developed a class of crosslinked norbornenes polymers for waveguide applications in datacom markets. The polymers can be formed by solvent-less polymerization under ambient environmental conditions. Using our monomer toolbox, we have the capabilities of tailoring optical, thermal and mechanical properties. The current preferred core and cladding system has low transmission loss (<0.1 dB/cm at 515-870 nm), wide spectral range (visible and near IR), low birefringence (Δn (in plane) $<10^{-5}$, Δn (out of plane) $<10^{-3}$ at 820 nm), consistent difference in index over a wide temperature range, long-term thermal stability (>2000 hours at 125 ºC), high glass transition temperature (>280 °C), and low moisture absorption (<0.1%). For the ease of fabrication of waveguides, the materials are designed to fit into economical conventional molding technique and several variations therefrom. Fabrication of optical waveguides (rib guides and isolated channel waveguides) has been demonstrated using several techniques, one of which has the potential of mass production of waveguides in a continuous film line. The optical transmission loss of the waveguides fabricated using this novel technique is 0.14 dB/cm at 820 nm. Further optimization of this fabrication approach and the study of thermal stability of the waveguides fabricated using this particular technique is still in progress. We envision that our waveguide polymer system

has the potential of mass production of low-cost and high-performance optical waveguides as reliable components for integrated optical devices used in the datacom market.

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