

Nanolayer polymeric optical films

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ABSTRACT *Coextruded films have been made that consist of several hundred alternating layers of two or three polymers having different refractive indices. With layer thicknesses of the order of 100 nm, these films cause optical interference of light waves and can reflect selected portions of the ultraviolet, visible, and infrared spectrum. All-polymeric interference films possess novel properties compared to vacuum deposited dielectric multilayers. Elastomeric film was made which reversibly changes reflected wavelengths with stretching and relaxation. Non-absorbing, birefringent interference polarizing film was made using polymers having different stress optical coefficients. A three component nanolayer film that reflects solar infrared wavelengths and transmits visible light was demonstrated.*

KEYWORDS

Coextrusion
Films
Interference
Multilayers
Optical
scattering
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Multilayer coextrusion of film and sheet containing as many as seven layers of three or more polymers is now common for many packaging applications. For cast film, sheet, and coatings with more than two or three layers, the feedblock method of flat die coextrusion remains the preferred technology because of its simplicity and versatility. With the feedblock method, molten polymers from individual extruders are subdivided and arranged into a multilayer melt stream that is coextruded through a conventional single manifold flat die (1). The method can be used to coextrude films having several hundred alternating layers of two or more polymers with individual layer thicknesses in the order of the wavelength of light (2).

One of the more unusual properties of these films is their interaction with light when the alternating layers have different refractive indices. Light waves reflecting from the many interfaces experience constructive (and destructive) interference and the film

exhibits vivid iridescence (3). Such films have been commercialized for decorative applications (4).

More recently, we have begun to explore some other potential applications for all-polymeric optical interference films. Compared to vacuum deposited dielectric multilayer interference stacks, polymer layers do not corrode and the film can be tough and thermoformable. Furthermore, there is no metal waste. Elastomeric interference films can also be made. Birefringent properties of polymers can be used to make non-absorbing light polarizers. Three-component polymer films can be coextruded which reflect solar infrared wavelengths while transmitting the visible portion of the spectrum.

This paper discusses some early stage development of these all-polymeric interference films.

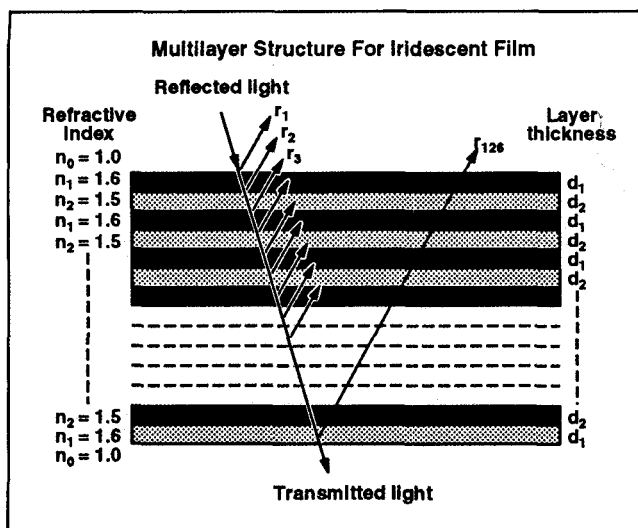
Optical theory

The science of thin film optics has been thoroughly developed (5, 6) and

has been applied to multilayer polymeric films (7, 8). No attempt will be made here to discuss detailed optical theory, except to summarize some convenient design equations and parameters useful in predicting performance. We have found the MacLeod thin film optics software package to be a useful tool in calculating detailed spectra for specific multilayer designs (9).

Figure 1 shows a schematic cross section through a multilayer film. It consists of alternating layers of polymers A and B, which have refractive indices of 1.6 and 1.5, respectively. Light is reflected from each of the layer interfaces (multiple reflections are not shown for clarity). Phase changes in light waves propagating through layers of different refractive indices result in constructive reinforcement of certain reflected wavelengths with transmission of complementary wavelengths. The reflected wavelength is a function of angle of incidence, ϕ , which gives rise to the play of colors from iridescent films.

1. Reflection of light from interfaces of multilayer film



For normal incidence of light from a uniform AB multilayer film, the reflected wavelength, λ , can be calculated from the sum of optical thicknesses for a repeat unit, where optical thickness is the product of refractive index and physical layer thickness.

$$\lambda_M = (2/M)(n_A d_A + n_B d_B) \quad (1)$$

where

M = order of reflection, 1,2,3...

n = refractive index

d = layer thickness

The amount of reflected light at each interface is determined by the difference of refractive indices as given by Eq. 2:

$$R = [(n_A - n_B)/(n_A + n_B)]^2 \quad (2)$$

where

R = reflectance

For polymers, the refractive index mismatch is small compared to vacuum deposited dielectrics, but the small reflectance from each interface is compensated by a large number of layers in these films.

Bandwidth, or span of reflected wavelengths, increases with wavelength, refractive index mismatch, and is strongly dependent on layer thickness gradient through the film. Non-uniform layer thicknesses result in broadband reflectance. Current

coextruded nanolayer films have layer thickness gradients and reflect broad bands.

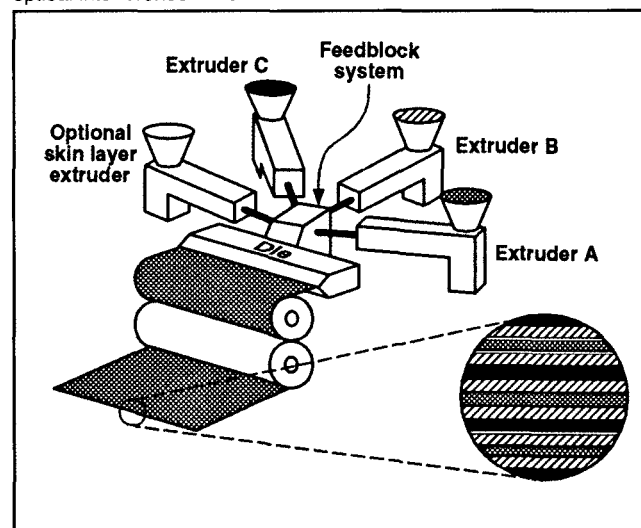
Finally, higher order reflections occur at multiple integer fractions of the first-order reflected wavelength. The intensity of these higher order reflections is determined by the ratio of optical thicknesses, f . For a two-component film having an AB optical repeat unit, this ratio is calculated from Eq. 3:

$$f = n_A d_A / (n_A d_A + n_B d_B) \quad (3)$$

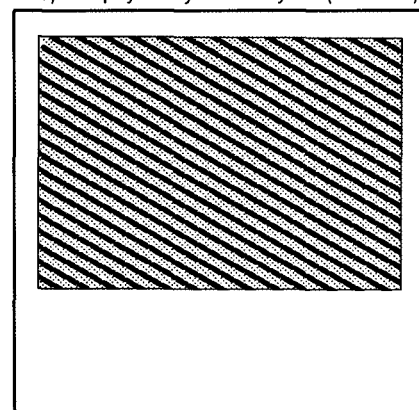
Some degree of control of higher order reflectance can be exerted by controlling optical thickness ratio, e.g., with equal optical thicknesses, $n_A d_A = n_B d_B$, all even order reflections can be suppressed. With an AB optical thickness repeat unit, it is not possible to suppress two successive higher order reflections. Three-component films having an optical repeat unit of ABCB can suppress successive higher orders and a design which suppresses three successive higher order reflections will be described later.

An electron micrograph through part of the cross section of a 657-layer film consisting of alternating layers of polycarbonate, RI = 1.59, and poly(methylmethacrylate), RI = 1.49, is shown in Fig. 2. The micrograph shows the degree of layer uniformity and interface smoothness which can be obtained in nanolayer coextrusion.

3. Schematic of laboratory coextrusion line used to make nanolayer optical interference films



2. Electron micrograph through a partial cross section of a 657-layer film consisting of alternating layers of polycarbonate (RI = 1.59) and polymethylmethacrylate (RI = 1.49)

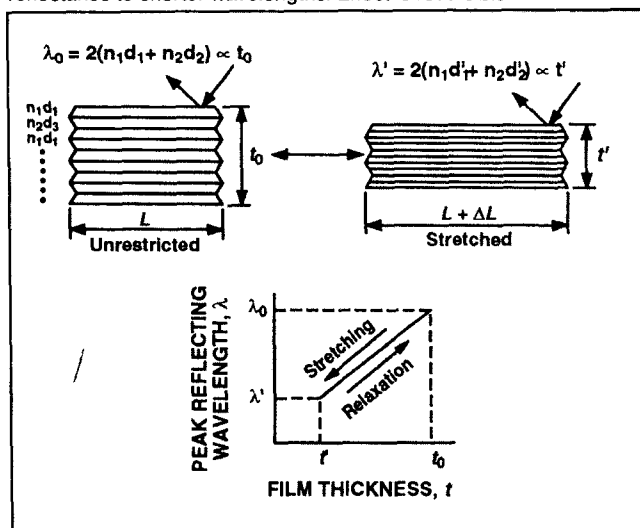


Coextrusion of nanolayer films

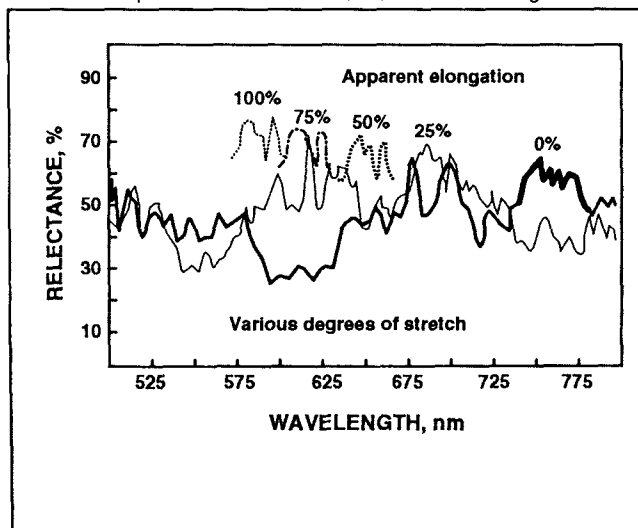
Current coextruded nanolayer films exhibit nonuniform spectral reflectance in the plane of the film caused by nonuniformity of layers through film thickness and across the width and length of the film. Film thickness variation, individual layer thickness variation, and interface distortions all contribute to the distorted reflectance spectra of the films as produced.

Since most structural nonuniformity can be traced to processing, rigorous process control will be required to minimize these variations. The degree of spectral reflectance uniformity possible is unknown at this time. Use of melt pumps to control volumetric extrusion rates, static mixers to

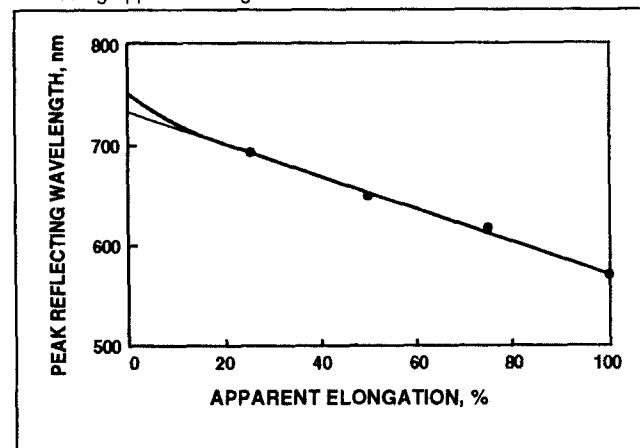
4. Stretching elastomeric interference film thins layers to shift reflectance to shorter wavelengths. Effect is reversible.



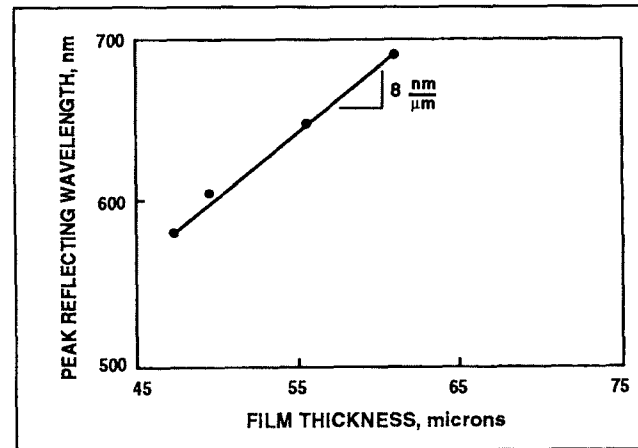
5. Reflectance at various degrees of stretch. For clarity only characteristic peaks are shown at 50, 75, and 100% elongation.



6. Decrease in characteristic peak reflecting wavelength with increasing apparent elongation



7. Dependence of peak reflecting wavelength with film thickness



minimize melt temperature nonuniformities, and computer control are presently being studied or planned. New die designs will be evaluated. Careful control of draw down and cooling outside the die will need to be studied to minimize film thickness variations which shift reflectance bands. Rheological properties of component polymers need to be carefully matched to minimize flow instabilities.

Ultimate development of nanolayer films may challenge the best state-of-the-art process technology and will probably necessitate innovations. The extent to which technology develops will be determined by potential applications and their requirements.

While current laboratory equipment falls far short of the ultimate,

it was used to demonstrate early stage feasibility of three types of nanolayer optical interference films to be described later.

Figure 3 is a schematic of the laboratory coextrusion line. Three extruders ranging from 1 1/4 in. (30 mm) to 1 3/4 in. (43 mm) are used to feed molten polymers into a feedblock which subdivides and arranges layers into an ABCB layer repeat sequence. The ratio of layer thicknesses is controlled by relative volumetric pumping rates. A fourth extruder is used to apply thicker skin layers to the film surfaces.

Skin layers can be the same polymer as one of those used in the core or a different polymer can be used. Skin layers provide protection to the thin core layers during processing to

minimize layer distortions caused by flow instabilities (10). They can also provide mechanical strength, UV protection, or a suitable surface for subsequent lamination.

The combined melt stream is coextruded through a 12-in. (300 mm), single manifold, flat-film die and drawn and cooled on chill rolls before winding.

Elastomeric interference films

Thermoplastic elastomers of differing refractive index can be coextruded into films whose reflected wavelengths change reversibly with stretching and retraction because of reversible change in layer optical thicknesses, as shown in Fig. 4 (11,

12). In addition to exhibiting interesting decorative effects, the film can potentially act as a tunable filter spanning wavelengths from the near infrared, through the visible, into the ultraviolet spectrum, which is not possible by conventional vacuum-deposited dielectric stacks.

Spectra for a two-component, 769-layer film are shown for 0, 25, 50, 75, and 100% apparent elongation. The spectral peaks move to shorter wavelengths with stretching and thinning of layers, as shown in Fig. 5, and return to substantially the original reflectance after retraction. A plot of the characteristic peak wavelengths shows linear response to elongation (Fig. 6) and film thickness (Fig. 7). There is insufficient birefringence to introduce significant polarization effects.

Broad band elastomeric interference films could be potentially developed for sensors (pressure, strain, inflation), adjustable solar reflecting films for greenhouses, etc., as well as for obvious decorative effects such as stretchable fabrics, balloons, and the like.

Birefringent polarizers

Up to now, the refractive index of polymers used in nanolayer coextruded films has been treated as isotropic. In addition to some dependence of refractive index to wavelength (dispersion), the refractive index of many polymers can be strongly dependent on molecular orientation.

A uniaxially oriented polymer film will have one refractive index in the direction of stretch and another perpendicular to that direction (birefringence). The magnitude of change in refractive index with stretching stress and its direction (positive or negative change) is given by the stress optical coefficient for the polymer. This anisotropic optical behavior of polymers can be exploited to make birefringent polarizers.

By choosing an appropriate pair of polymers having different stress optical coefficients (SOC), reflected light can be polarized.

An example is shown in Fig. 8, where polymer A has a large positive SOC and experiences a strong increase in refractive index in the direction of stretch accompanied by a decrease in the transverse direction.

Polymer B is chosen with a different SOC so that a specific stretch temperature and draw ratio results in a wide mismatch in refractive index in the direction of stretch and negligible mismatch in the transverse direction.

Light waves propagate in all directions along an incident ray and can be resolved into two orthogonal components. As shown in Fig. 9, the component aligned in the direction of stretch sees a mismatch in refractive index, and wavelengths which are constructively interfered are reflected as polarized light. The component aligned perpendicular to the stretch direction sees a negligible refractive index mismatch and therefore is transmitted. In addition, both components of light, at wavelengths that do not constructively interfere, are transmitted.

Two polymers similar to the example of Fig. 8 were coextruded into 657-layer films, cooled, and subsequently stretched uniaxially at a temperature above the glass transition temperatures of the two polymers. Transmission of polarized light was measured, and the spectra in the direction of stretch and the transverse direction are shown in Fig. 10. Loss of transmission in the direction of stretch is by interference reflection of the incident polarized beam. The polarized beam is transmitted in the transverse direction as there is little mismatch in refractive index.

While the polymers used were not optimized, the feasibility of a birefringent polarizer which does not absorb light as do dichroic crystal polarizers has been demonstrated. Broad band polarization across the entire visible spectrum should be possible by using an appropriate layer thickness gradient.

Suggested applications for these novel nonabsorbing, nanolayer, polymeric birefringent polarizers include beam splitters and glare reduction. Potential development will be stimulated by imaginative, commercially significant applications.

Infrared reflecting film

It is possible to coextrude nanolayer films that reflect near infrared wavelengths (13). One potential application for such films is to reject solar infrared radiation by reflection and reduce heat load in buildings and

vehicles. Most solar infrared energy is transmitted between 800 and 1600 nm, representing approximately 50% of total solar energy (14). While two-component AB nanolayer films can be designed to reflect these wavelengths, troublesome higher order reflections occur in the visible, leading to iridescence.

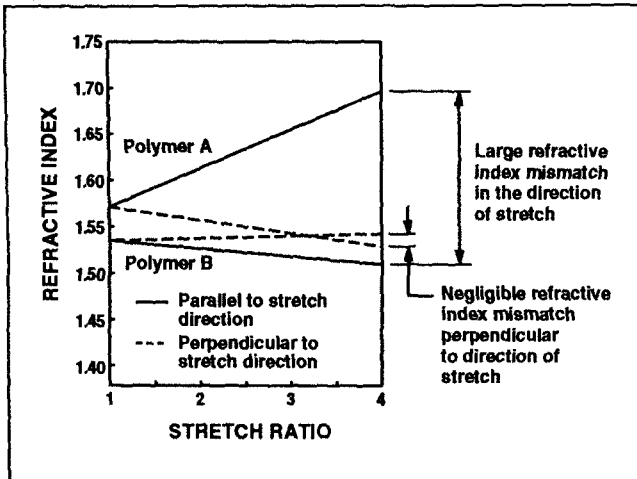
These higher order reflections can be suppressed by introducing a third polymer into an ABCB—nanolayer film structure. In one specific design, Thelen proposed a periodic multilayer stack of three vacuum deposited dielectric materials which suppressed three successive higher orders (15). The ratios of optical thicknesses in the ABCB repeat unit are specified to be 1/3, 1/6, 1/3, 1/6, and the refractive indices are chosen so that $n_B^2 = n_A n_C$. The first-order reflectance of a uniform layer stack is given by Eq. 4:

$$\lambda_1 = 2(n_A d_A + 2n_B d_B + n_C d_C) \quad (4)$$

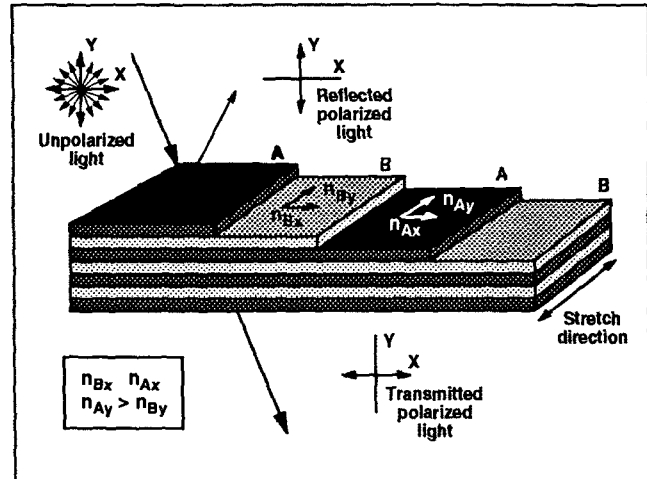
Second through fourth orders are suppressed by this design. A uniform stack of multilayers will reflect a relatively narrow bandwidth, and a gradient in layer thicknesses is required to reflect the 800 to 1600 nm solar infrared range. A schematic design is shown in Fig. 11, and calculated spectra for a 464-layer film design with linear thickness gradient is shown in Fig. 12. The spectra in Fig. 12 were calculated for $n_A = 1.636$, $n_C = 1.45$, with n_B chosen to be 1.54, 1.57, or 1.59. For all values of n_B which were used, first-order infrared wavelengths are reflected between about 800 and 1600 nm at an average reflectance of about 85%. The design transmits the visible wavelengths. Transmittance in the visible region decreases with deviations from the theoretical value of $n_B = (n_A n_C)^{1/2}$. Deviation in optical thickness from precise mathematical relationships may be permissible if a small amount of visible reflection is acceptable.

To experimentally verify the feasibility of coextruding such three-component films, a 657-layer film was made from two styrene-methylmethacrylate copolymers having refractive indices of 1.57 and 1.53, and polymethylmethacrylate with refractive index of 1.49. Relative reflectance was measured with an integrating sphere spectrophotometer and an aluminum coated reference mirror.

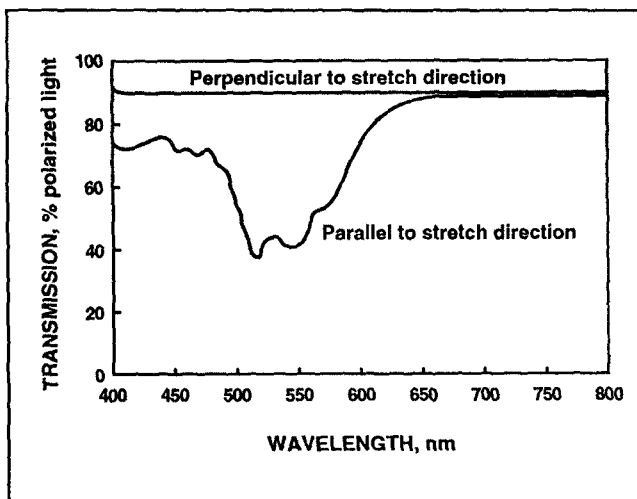
8. Change in refractive index with molecular orientation for two polymers of different stress optical coefficients



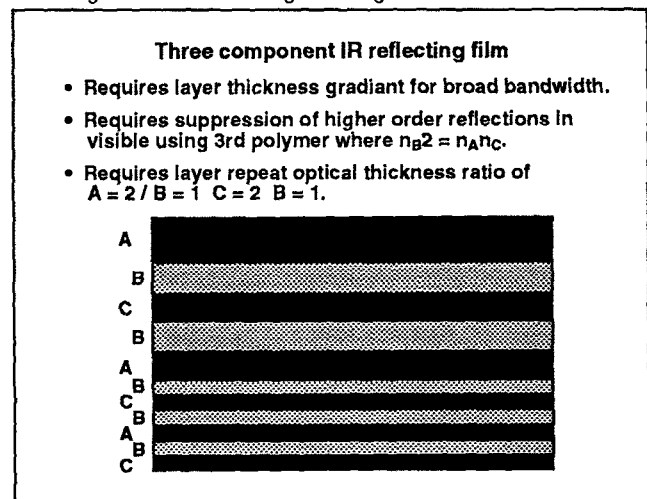
9. Schematic of uniaxially oriented film for birefringent polarizer



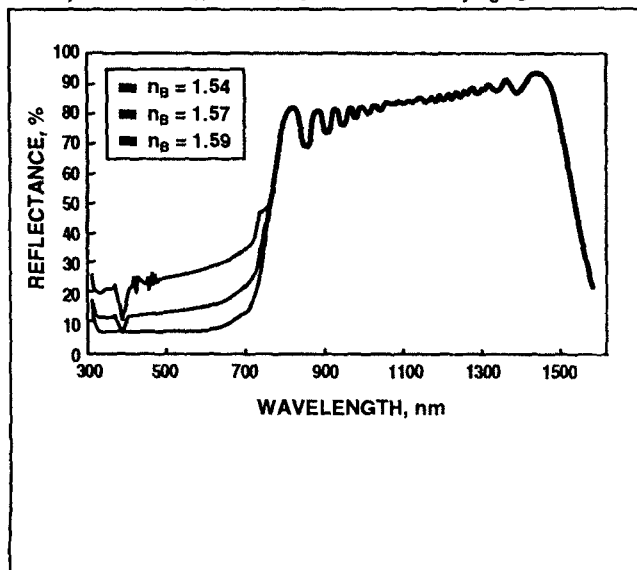
10. Transmission spectra of multilayer birefringent polarizer



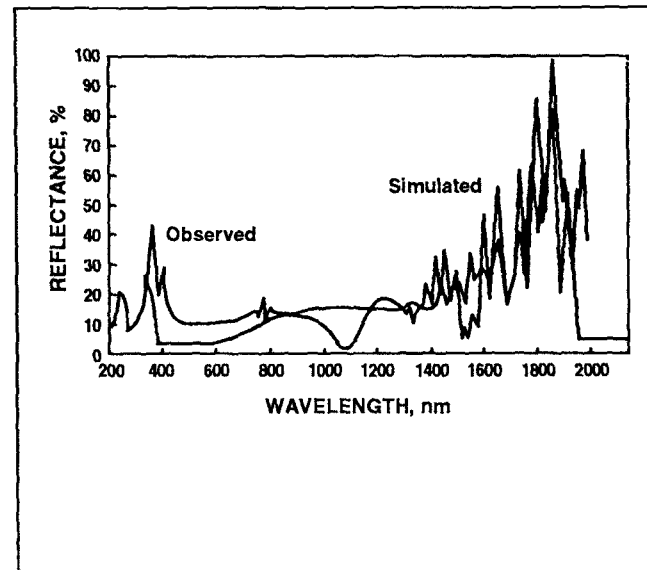
11. Example of a multilayer film designed to reflect solar infrared wavelengths while transmitting visible light



12. Effect of refractive index mismatch on visible reflectance for a 464-layer film with $n_A = 1.636$, $n_C = 1.45$ and a varying n_B



13. Observed and calculated reflectance for a 657-layer film



The measured spectrum of a typical sample is shown in Fig. 13. The first-order peak of about 80% relative reflectance occurs at 1900 nm. Absence of second-, third-, and fourth-order peaks at 1/2, 1/3, and 1/4 of the first-order peak is in agreement with theory. The expected fifth-order peak at $1900/5 = 380$ nm is seen. While this film had a relatively low mismatch in refractive index ($\Delta n_{\max} = 0.08$), which limits reflectivity and the layer thickness gradient was not optimized, it nevertheless demonstrates feasibility.

Although detailed layer thickness measurements were not made on this sample, a simulated spectrum was calculated from an assumed layer distribution from a typical prototype film layer distribution. The simulation shown in Fig. 13 has been mathematically smoothed over 25-nm bands to eliminate misleading sharp band structure. The actual and theoretical spectra are in remarkable agreement, particularly since the experimental film exhibits some layer distortions caused by flow instabilities.

Optimization of polymers for increased refractive index mismatch and rheology for processing, combined with control of layer thickness gradient will be necessary for these films to provide economical, effective solar energy management.

Conclusions

The feasibility of producing novel coextruded optical interference films has been demonstrated. Polymer selection and processing technology are used to obtain optical characteristics in the film that are difficult or impossible to achieve by conventional vacuum deposition of dielectric layers. These properties include elastomeric behavior and birefringence in addition to the more common attributes of polymers such as corrosion resistance, formability, etc.

Optical performance of these early developmental elastomeric interference films, birefringent polarizers, and three-component infrared reflecting films which are visibly transparent are in good agreement with

calculated spectra from thin film optical theory.

Rigorous process control will be required to obtain improved uniformity and reproducibility. The extent to which these unique films will be developed is dependent on their potential applications as tunable filters, birefringent polarizers, solar heat reflectors, etc., and new imaginative uses yet to be created.

Nothing herein is meant to grant or imply a license or freedom to practice under any patent of Dow or others. □

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