Light Controlling Properties of Highly Oriented Natural Rubber Latex Film

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A R T I C L E   I N F O

A B S T R A C T

Background: In this present work, acrylated rubber latex film with light-controlling properties was fabricated using monodisperse acrylate spheres and pre-vulcanized latex (PVL). The resultant film exhibited a reversible reflectance wavelength when highly oriented into high elongation upon interaction with incident light. Benefiting from the elastic characteristic of natural rubber latex, the film produced can withstand elongation up to 600% elongation to give various reflectance wavelengths at different strain levels. The results show that the light comtrolling properties of acrylated PVL film produced largely depends on the strain levels. This wavelength tunable property is attributed to the reduction of the spacing distance during the deformation. **Objective:** Proposes natural rubber latex, which is PVL, as a substitute for PDMS in fabricating elastic crystal films with both tunable wavelengths and considerable elongation properties. **Results:** The reflectance wavelength of the acrylated PVL film could be controlled by shifting the stop band to a shorter wavelength, mainly by adjusting the strain level during stretching. **Conclusion:** Natural rubber such as PVL can be used in fabricating films with wavelength-tunable properties upon high elongation.

INTRODUCTION

Photonic crystals have attracted interest as a light-sensitive material with light-controlling properties and reversible tuning characteristics. The interest in photonic crystals is attributed to their promising ability to show structural colors if their stop bands are located in the visible light region [1]. Propagation of light within the photonic crystal structure can be fully prohibited when they are trapped in a certain direction, depending on the photonic crystal structure and its refractive index contrast [2]. Due to this unique property, photonic crystals with tunable structural colors can be tuned by controlling various external stimuli, such as mechanical strain [3-6], refractive index [7], angle of incidence [8-9], magnetic field [10-11] and sphere size [12-13].

Among all of the elastic photonic crystals, polymer latex and rubber are the most widely used material for the elastomeric part of the crystal structure because of the ease of fabrication and the fact that they can be prepared inexpensively on a large scale. As a matter of fact, the elasticity of rubber and polymer latex makes it possible to tune the wavelength position by simply distorting and deforming this elastic part by means of stretching. Upon stretching, the spacing between sphere lattices in the elastic film change linearly with strain, resulting in a shifting of the wavelength produced by Bragg diffraction. Fudouzi *et al*. previously reported an elastic photonic crystal film consisting of a regular arrangement of polystyrene particles and a silicone elastomer filling the interstices in the polystyrene. The film was reported to exhibit structural color changes when elongated in the horizontal direction due to reduction of the sphere spacing in the longitudinal direction [14]. Similarly, Wohlleben *et al*. found out that the distance of the lattice spheres can be decreased by applying a stretching force to the film [15]. Jian Li and co-workers reported the fabrication of three-dimensional (3D) polymeric photonic crystals made from thermoplastic polyester elastomer (TPEE), which can be reversibly tuned at room temperature by stretching the crystal and recovering along the (111) plane [16-17]. Although strain deformation has been proven to be responsible for the wavelength tuning of elastic photonic crystal structures, sphere size is one of the important factors in determining the resultant wavelength region. For

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example, it is recommended that a sphere size of approximately 100 – 200 nm be used to target the wavelength region of visible light (380 nm -730 nm) [7, 18]. In contrast, a larger sphere size of approximately 700 nm can target the wavelength region of 1550 nm, approaching the IR region [9, 16].

As mentioned previously, the elastomeric part of elastic photonic crystal films is normally fabricated by polymer latex or rubber. For rubber, the most widely used type is polydimethylsiloxane (PDMS), a silicone rubber. PDMS is reported to be deformed reversibly and repeatedly without residual distortion, and it is also chemically stable, biocompatible, thermally stable, inexpensive, nontoxic and commercially available [5, 19]. Despite these numerous advantages, inconvenient processing and the relatively low elastic modulus of PDMS can lead to distortions of surface features with high aspect ratios. [20-21]. As an alternative, this paper proposes natural rubber latex, which is PVL, as a substitute for PDMS in fabricating elastic crystal films with both tunable wavelengths and considerable elongation properties. Acrylate spheres were incorporated with PVL to create refractive index differences along the film. When the film is highly stretched, the spheres are forced to arrange in an orderly manner along the strain direction, thus displaying wavelength tuning upon interaction of light.

Experimental Methods:
Materials and apparatus:

Pre-vulcanized latex (PVL) was purchased from Revertex Sdn Bhd (Malaysia). Acrylate monomer 99 % and potassium peroxodisulfate, which was used as an initiator, were purchased from Sigma-Aldrich Sdn Bhd (Malaysia) and used as received. Sodium stearate, which acts as an emulsifier, was purchased from Fisher Scientific Sdn Bhd (Malaysia). Surface morphology photographs were taken by scanning electron microscopy (SEM) with a field-emission scanning electron microscopic (Oxford Instrument). Stress-strain curves were measured by an Instron Tensile Tester (5900 series). Wavelength reflections were measured by an Ocean Optics mini spectrometer (USB 4000-VIS-NIR).

*Synthesis of monodisperse acrylate spheres:*

Acrylate spheres were self-synthesized using the emulsion polymerization method. In a typical synthesis, 180 ml of distilled water and 106 ml of acrylate monomer were added to a 1 L round-bottom, 5-neck flask. The monomer was heated first at a temperature of 60°C to remove the inhibitor. The initiator was potassium peroxodisulfate (KPO), the emulsifier was sodium stearate, and the medium was distilled water. The polymerization reactor consisted of a mechanical stirrer, a nitrogen gas inlet, and a thermometer to control the polymerization temperature. Acrylate monomer and distilled water were first introduced into the reactor and stirred for 30 minutes. The polymerization reaction started just after initiator feeding and lasted for 4 hours. During polymerization, the stirring speed and polymerization temperature were maintained at 700 to 750 rpm with a fixed temperature of 70 °C. After reaction, the mixture was filtered, and the resultant precipitation was dried at 60 °C in a vacuum oven for 5 hours.

Fabrication of acrylated latex films:

Natural rubber latex, PVL was mixed with the required amount of acrylate particles during slow electric stirring below 40 rpm to obtain composite latex. The mixture was stirred until a homogenous blend was obtained. The freshly prepared acrylate-latex mixture was then cast onto a rectangular glass substrate during the casting process. The mixture was cast by a drawdown rod to obtain a uniform thickness of acrylated latex film. The cast was left to dry overnight under laboratory conditions, yielding a thin, transparent film. The thickness of the acrylated PVL film produced is ≈ 500 μm.

Optical setup:

Basically, an optical analysis of photonic material normally involves lenses, amplifiers, monochromators and spectrometers [22]. For example, a spectrometer is the key instrument for many optoelectric measurements. In their research to measure the reflected wavelength of a stretched photonic crystal sheet, Privorotskaya *et al*. [23] have developed an optical setup consisting of a lens, a polarizer, fibers and a spectrometer to observe and measure the wavelength shift as a function of applied stretch. Fig. 1 depicts a schematic illustration of the optical setup employed in this work. This set-up simply consisted of a tensile tester to elongate the film, two different lenses for focusing the light beams and a spectrometer to measure the reflected wavelength. The optical analysis was performed in the following manner. First, both ends of the film were positioned between the two grips of the tensile tester machine. Such a setup results in highly oriented acrylate spheres due to the high elongation of the stretched film. While stretching, an incident light was introduced to the sample. The reflectance wavelength, incident angle and percent elongation during stretching were measured and recorded.
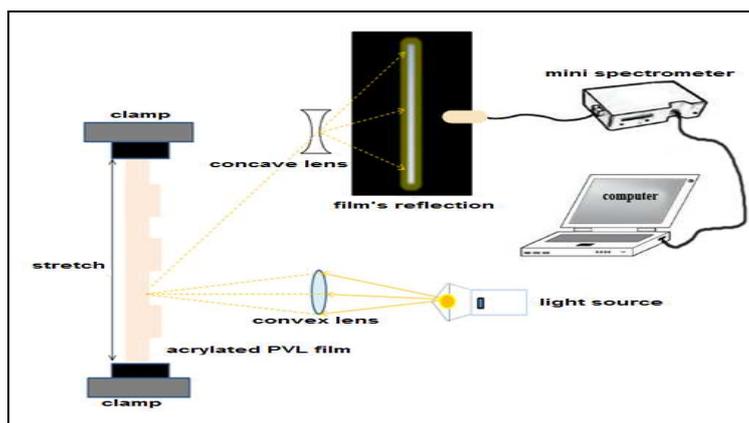
Fig. 1: Schematic illustration of the optical setup employed to tune the wavelength of acrylated PVL films by strain deformation.

RESULTS AND DISCUSSION

Acrylate incorporation:

Acrylate spheres were self-synthesized by emulsion polymerization. The elasticity of the acrylated PVL film largely depends on the proportion of monomer incorporated. The films were prepared with different amounts of acrylate and are summarized in Table 1. The film with an acrylate content less than 2.5 % exhibited good elongation properties but had a poor structural color due to the large gap between the sphere units. In contrast, the film prepared with an acrylate content greater than 2.5 % was less elastic and easily broken at low stress. Upon investigation of the tensile properties and during the wavelength tunability analysis, the film prepared from 2.5 % acrylate content was selected for further investigation because it has good tensile properties and offers better wavelength tuning than the other films.

Table 1: The effect of acrylate content on the mechanical strength and wavelength tuning of acrylated PVL films

| Acrylate Content (%)		
	Mechanical Strength	Wavelength Tunability
< 2.5	good	poor
2.5	good	good
> 2.5	frangible	good

Surface morphology:

The microstructures of the as-prepared films were investigated by SEM. Figs. 2a and b present typical SEM images taken on the surface of an acrylated PVL film assembled from acrylate spheres. An ordered structure of acrylate spheres can be seen arranged on the entire surface of the latex film. From these two images, it can be concluded that the spheres were embedded in the elastic surface of the PVL film. In Fig. 2a, it can be seen that an ordered structure of acrylate spheres was separated into several domains by the PVL rubber. Viewed at a higher magnification of 100K, Fig. 2b shows that the spheres are spherically shaped and separated by a small distance. Further observations of the images from the SEM analysis indicate that the spheres had an average diameter, D, of 513 nm.

Acrylate spheres that are arranged on the surface of a latex film may create a grating spatial period, Λ, which can easily be described as the spacing distance between the spheres. The purpose of introducing grating into an elastic cavity is to integrate a wavelength-selective structure that is responsible for tuning the color of photonic crystals under strain upon interaction with light [24]. Therefore, during stretching, acrylate spheres may be arranged in an orderly manner according to the stretching direction and then become closer to one another. When light is introduced to the stretched film, the reduction in the sphere distance may reflect light at a shorter wavelength. The wavelength values may change linearly with the spacing distance. As the spheres get closer, the wavelength gets shorter and vice versa. Figs. 3(a) and (b) show transverse and cross-sectional diagrams of the acrylated PVL film when unstretched and stretched. Notice that the spacing distance between spheres of the stretched film was shorter than that of the unstretched film.
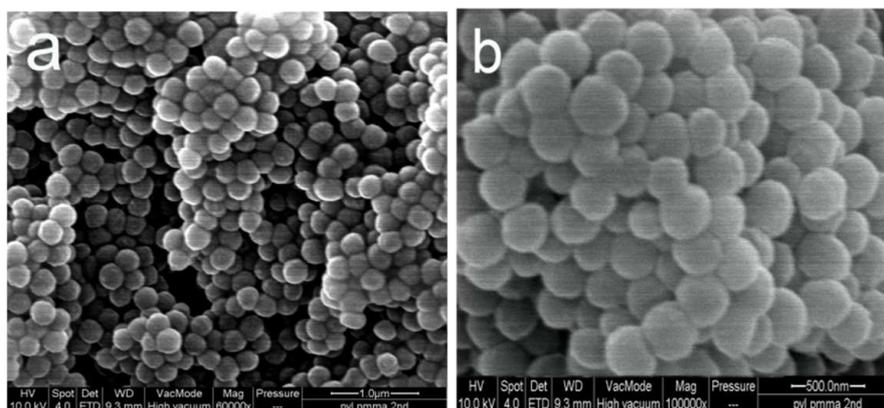
Fig. 2: Typical SEM images of acrylated PVL film surfaces at different magnifications: (a) 60 000x; (b) 100 000x.
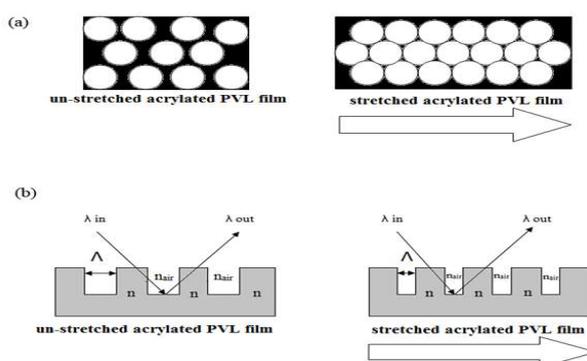

Fig. 3: Transverse (a) and cross-sectional (b) diagrams of unstretched and stretched films.

The grating's spatial period, Λ, may create wavelength-selective structures when the film is introduced to light.

Wavelength tuning under strain deformation:

The reflectance wavelength of the acrylated PVL film could be controlled by shifting the stop band to a shorter wavelength, mainly by adjusting the strain level during stretching. Fig. 4 shows the reflection spectra measured on the films with different stretch levels. Using a miniature spectrometer for measuring, the reflectance wavelength was found to shift from 584.25 nm at 200 % elongation to 560.92 nm at 400 % elongation, and it continued to decrease to 467.47 nm with the increasing of the stretch level to 600 % elongation. From this analysis, it is found that wavelength shifting is due to the reduction of the spacing distance, *d*, in response to the increasing levels of strain.
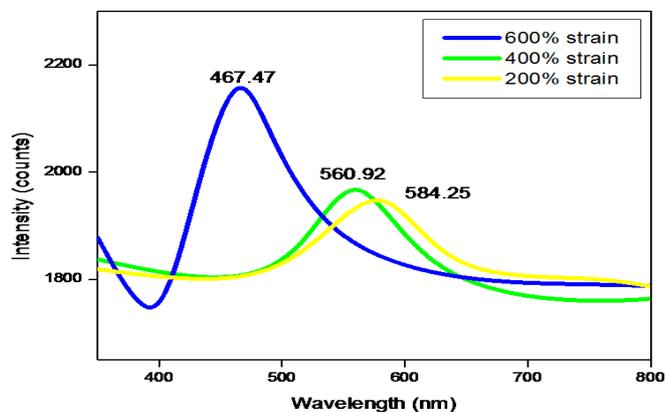
Fig. 4: Shifting of the reflectance wavelength as a function of different stretch levels.

The reflectance wavelength, λ, is found to be closely related to the decreasing of the spacing distance, *d*, with respect to the elongation of the film. This is further explained by Bragg's equation and Snell's law,

$$\lambda = 2d\sqrt{n_{eff}^2 - \sin^2\theta}, \tag{1}$$

where *d* is the spacing distance of the spheres, n_{eff} is the effective refractive index, and θ is the angle of incident light on the sample along the [111] direction. The effective refractive index, n_{eff}, is given by $n_{eff} = n_{polymer}\ f_{polymer} + n_{air}\ (1 - f_{polymer})$, where n_{air} and $n_{polymer}$ are the refractive indices of air and acrylated PVL, respectively, and $f_{polymer}$ is the volume fraction occupied by acrylate spheres in the PVL film. Because $n_{air} \approx 1$, $n_{polymer} \approx 1.54$, and for an ideal close-packed structure, $f_{polymer} \approx 0.74$; thus, n_{eff} is calculated to be 1.40.

It is found that the reflectance wavelengths at 200 %, 400 % and 600 % strain measured by a spectrometer are 584.25, 560.92 and 467.47 nm, respectively. Meanwhile, the values of the incident angle measured at these three strain levels and wavelengths are 5°, 20° and 50°. Therefore, by using collected data for the reflectance wavelength and incident angle measurements, the values of the spacing distance, *d*, at 200 %, 400 % and 600 % strain can be calculated using equation (1) as follows:

(a)   200 % strain

$$584.25 = 2d\sqrt{1.40^2 - \sin^2(5°)}$$
$$d = 209$$

(b)   400 % strain

$$560.92 = 2d\sqrt{1.40^2 - \sin^2(20°)}$$
$$d = 207$$

(c)   600 % strain

$$467.47 = 2d\sqrt{1.40^2 - \sin^2(50°)}$$
$$d = 199$$

From the above calculations, it is proven that there was a reduction in the spacing distance, *d*, when the film was subjected to strain deformation. Similar findings were reported by previous researchers; the reflection wavelength position decreases with increasing applied stretching due to the decreases of the spacing distance parallel to the film surfaces [25-26]. Therefore, it can be concluded that wavelength shifting is due to the decrease of the spacing distance of acrylate with respect to the elongation of the film.

Conclusions:

In conclusion, it has been shown that a natural rubber such as PVL can be used in fabricating films with wavelength-tunable properties upon high elongation. To obtain good tensile and wavelength tunability properties, a suitable amount of acrylate needs to be incorporated with PVL. The reflectance wavelength of the highly oriented film can be changed by simple mechanical stretching. Calculations using the Bragg-Snell Law prove the reduction of the spacing distance between acrylate spheres, which is responsible for producing shorter wavelengths with increases in the strain level. Further investigation can broaden the potential of natural rubber as a main material in the fabrication of many photonic devices in engineering applications.

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