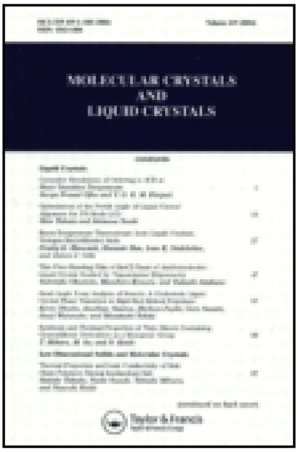

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Deformable Viscoelastic Cholesteric Films with Nanoparticles

Petr V. Shibaev [a] , Cristina Schlesier [a] , Eckhard Hanelt [b] & Michael Manevich [c]

[a] Department of Physics, Fordham University, Bronx, NY, USA
[b] Consortium fuer Elektrochemische Industrie GmbH Zielstattstr, Muenchen, Germany
[c] Lev Institute-JCT, Jerusalem, Israel

Version of record first published: 30 Jun 2011

To cite this article: Petr V. Shibaev, Cristina Schlesier, Eckhard Hanelt & Michael Manevich (2011): Deformable Viscoelastic Cholesteric Films with Nanoparticles, Molecular Crystals and Liquid Crystals, 545:1, 53/[1277]-57/[1281]

To link to this article: http://dx.doi.org/10.1080/15421406.2011.571973

Mol. Cryst. Liq. Cryst., Vol. 545: pp. 53/[1277]–57/[1281], 2011

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2011.571973

Deformable Viscoelastic Cholesteric Films with Nanoparticles

PETR V. SHIBAEV,[1] CRISTINA SCHLESIER,[1] ECKHARD HANELT,[2] AND MICHAEL MANEVICH[3]

[1]Department of Physics, Fordham University, Bronx, NY, USA
[2]Consortium fuer Elektrochemische Industrie GmbH Zielstattstr, Muenchen, Germany
[3]Lev Institute-JCT, Jerusalem, Israel

Large spectral shifts of the selective reflection band and color changes are achieved in highly viscous mixture of cholesteric polymers and low molar mass liquid crystals filled with nanoparticles and subject to mechanical deformations. The color of the material changes instantaneously during deformation; the time for the color to be completely restored increased with the viscosity of the polymer mixture. The viscosity increases with increasing concentration of polymer or nanoparticles. These properties of the material were explored in building a highly sensitive mechanical sensor.

Keywords Cholesteric; color; deformation; nanoparticles; sensor; viscoelastic

1. Introduction

Highly viscous cholesteric liquid crystals (CLCs) sensitive to mechanical deformation, stretching, and shear were recently studied in [1–4]. In these materials high viscosity plays a crucial role in determining their peculiar mechanical response. Highly viscous CLCs can be obtained by mixing polymer CLCs and low molar mass nematic liquid crystals. The viscoelasticity of such materials can be controlled by changing the ratio between polymer and liquid crystal. The gained viscoelasticity allows for deformation to be visualized by deformed helical axis almost simultaneously. Thus, these materials are almost ideally suited for building a variety of mechanical sensors and for visualizing a distribution of stress. It is well known that the color of a cholesteric sample and the position of the center of the selective reflection band (SRB) is determined by $\lambda = nP$ (where P is the helical pitch of the chiral liquid crystal and $n = (n_e + n_o)/2$ is the average refractive index of the cholesteric planes [5]). While in common thermotropic low molar mass liquid crystals the alteration of helical pitch quickly vanishes due to low viscosity and short relaxation time (proportional to $\frac{\gamma P^2}{K} = 10^{-2} - 10^{-3}$ s), highly viscous cholesteric materials relax slowly, with typical maximum relaxation time c.a. 10^2 s.

Address correspondence to Petr V. Shibaev, Department of Physics, Fordham University, 441 East Fordham Rd., Bronx, 10458, NY, USA. E-mail: shibpv@yahoo.com

It is interesting to compare the elastic properties of highly viscous cholesteric liquid crystals with the properties of cholesteric elastomers that recently attracted considerable attention. Cholesteric elastomers can respond reversibly to different types of deformation by changing the helical pitch and keeping these changes in the deformed state [6–8]. Finkelmann *et al.* synthesized and studied cholesteric elastomers under uniaxial and biaxial stress [6]. Terentjev *et al.* studied deformation of cholesteric elastomers and changes in their photonic band gap [7,8]. Cholesteric elastomers represent a group of chiral polymers, whose behavior, in theoretical terms, can be described by purely elastic deformation. Highly viscous cholesteric liquid crystals are viscoelastic materials and cannot be described in terms of purely elastic model.

The development of viscous cholesteric materials filled with nanoparticles is a new venue of research that may lead to a successful creation of novel highly sensitive mechanical sensors and smart ferromagnetic fluids.

In this paper we briefly discuss some properties of highly viscous CLC materials filled with nanoparticles that, we believe, make them very attractive for a new generation of mechanical sensors or materials able to visualize mechanical stress.

2. Results and Discussion

Highly viscous CLCs were prepared by mixing 70–80 wt.% of silicone-based cholesteric liquid crystals C4745, C4754 or C4768 (Wacker Co) and 30–20 wt.% of a nematic liquid crystal, MBBA (Sigma-Aldrich Co.) (see Fig. 1 for chemical

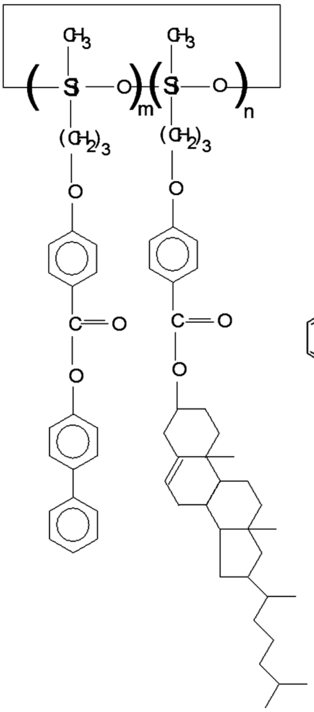

Figure 1. Chemical structure of the components of the mixture.

structures of liquid crystalline compounds). Nanoparticles of iron(III) oxide (nonspherical nanoparticles), nickel (spherical) and tin oxide (spherical) were used, the average size of the particles was less than 70 nm. In order to increase compatibility of nanoparticles (iron oxide and tin oxide) with polymer mixture, the particles were treated in oleic acid. The concentration of chiral groups in the Wacker polymers decreases from C4745 to C4768, leading to a longer selective reflection wavelength (450 nm, 540 nm and 660 nm, respectively). This allows to prepare mixtures with the selective reflection band centered at any point within the visible spectrum. The viscosity of the polymer/MBBA/nanoparticle composite was measured either by the vibrating fork or by the two plates methods and was found to significantly increase with polymer concentration. The composite was placed between two glass plates, the varying pushing force induced the motion of the upper plate with respect to the lower one with constant velocity. The effective viscosity can be estimated from the equation

$$\gamma = \frac{Fd}{A\nu}, \tag{1}$$

where d is the distance between plates, F is the pushing force, A is the area of the sample, v is the velocity of upper plate motion. The properties of polymer/MBBA system and dependence of viscosity on concentration of MBBA was studied in previous publications [1–3]. Here we mainly focus on the properties of composites filled with nanoparticles.

The color of the sample changed significantly when the shear deformation was applied to the sample placed between two glass plates with one of them shifting with respect to another. Color restoration takes a longer time than in the case of deformation of the same mixture without nanoparticles. Color is completely restored after deformation is terminated and the sample relaxes.

There are two major effects that contribute to the color changes in the sample at relatively low and high viscosities.

Figure 2 displays the dependence of relative viscosity measured by the two plates methods as a function of nanoparticles concentration. Relative viscosity is shown with respect to the mixture consisting of 65% of Wacker polymer and 35% MBBA. It is easy to see that viscosity increases significantly with concentration of nanoparticles. Nanoparticles do not change the helical pitch of the mixture, but they change the color of the mixture and the visual appearance of aligned cholesteric films. Thus, by varying the concentration of polymer and nanoparticles, it is possible to independently adjust both the helical pitch and the viscosity to any given value and study samples with the same helical pitch and different viscosities.

It is important to distinguish two regions of nanoparticle concentrations (below and above 10% in Fig. 2). At low concentrations (below 10%) the color of the samples is mostly determined by the selective reflection from the helical structure, and viscosity depends almost linearly on increasing nanoparticle concentrations following the dependencies described in [9]. Due to the higher viscosity of the samples the aggregation of ferromagnetic and non-magnetic particles is greatly suppressed. Comparison of highly viscous CLCs with common CLCs (mixture consisting of MBBA and chiral dopant CB15 (from Merck), or mixture of cholesterol derivatives) reveals that time needed to observe the aggregation of ferromagnetic particles increases at least by a factor of 100. In this concentration range nanoparticles tend to be located at oil-streaks or form suprahelical organization [10].

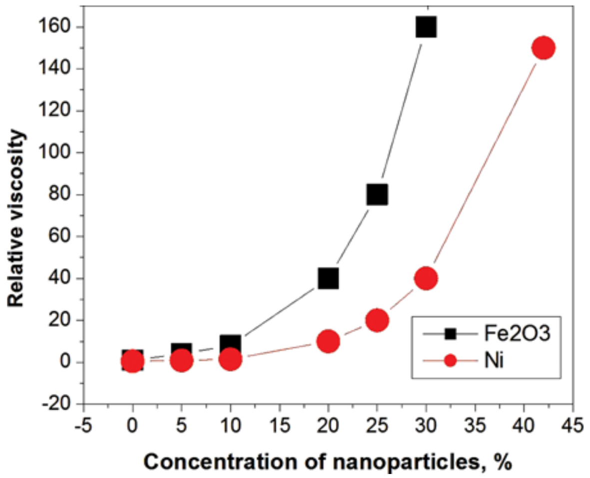

Figure 2. Viscosity of the sample as a function of nanoparticles' concentration. (Figure appears in color online.)

At higher concentrations of nanoparticles the color of the sample was mostly determined by the light absorption of the nanoparticles. The color of the CLC mixture (selective reflection band is positioned near 540 nm) with ferromagnetic iron oxide is brown; the color of the sample with indium tin oxide is yellow; the color of the sample with nickel particles is bright blue. In spite of the dominance of the color determined by light absorption, even slight shear deformation of the sample leads to significant color changes due to increased light scattering resulting from a sudden breakage of the cholesteric structure, elongation and distortion of cholesteric domains, and the development of new defects. The intensity of light scattering during deformation increases significantly. A response of a mechanical sensor that is able to measure small deformations by using scattered light is given in Figure 3. The LED

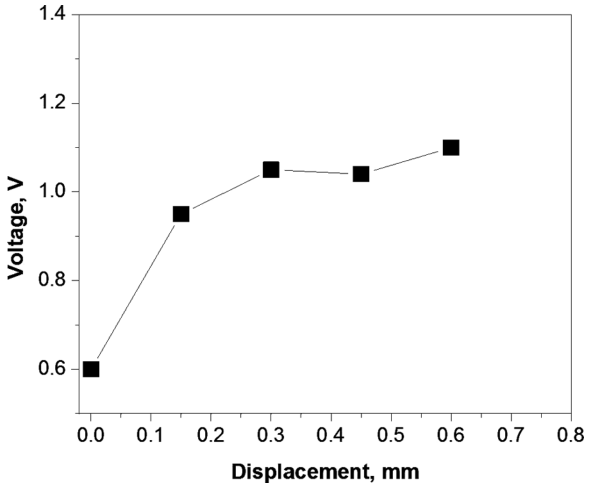

Figure 3. Output voltage on photodiode circuit as a function of upper glass displacement.

shines light at the sample, which is collected by a photodiode placed at the angle different from the angle of incidence of illuminating light. The small deformation (corresponding to a 0.1 mm shift of upper plate with respect to the lower one) results in a significant electrical signal on the photodiode.

Conclusions

Novel cholesteric composites based on mixtures of Wacker polymer, MBBA, and nanoparticles that provide light absorption in different parts of the spectrum are highly sensitive to mechanical deformation. The color of the planar composite depends on the absorption of nanoparticles and the position of the selective reflection band of polymer and nematic. Aggregation of nanoparticles inside highly viscous composites is suppressed in the best cases by a factor of c.a. 100. The viscoelastic mechanical response of the samples including composites allows to build sensors responding to small shear deformations.

References

[1] Shibaev, P. V., Rivera, P., Teter, D., Marsico, S., Sanzari, M., & Ramakrishnan, V., & Hanelt, E. (2008). *Opt. Express*, *16*, 2965.

[2] Shibaev, Petr V., Uhrlass, R., Woodward, S., Schlesier, C., Ali, Md R., & Hanelt, E. (2010). *Liquid Crystals*, *37*, 587.

[3] Shibaev, Petr V., Woodward, S., Schlesier, C., & Hanelt, E. (2010). *Liquid Crystals*, *37*, 1601.

[4] Schmidtke, J., & Terentjev, E. M. (2010). *Appl. Phys. Lett.*, *96*, 151111.

[5] Chandrasekhar, S. (2004). *Liquid Crystals*, Cambridge University Press, second edition.

[6] Finkelmann, H., Kim, S. T., Muñoz, A., Palffy-Muhoray, P., & Taheri, B. (2001). *Advanced Materials*, *13*, 1069.

[7] Cicuta, P., Tajbakhsh, A. R., & E.Terentjev, M. (2002). *Phys. Rev. E.*, *65*, 051704.

[8] Terentjev, E. M., Warner, M., & Mao, Y. (2001). *Phys. Rev E*, *64*, 041803.

[9] Sudduth, R. D. (2003). *Materials Science and Technology*, *19*, 1181.

[10] Mitov, M., Bourgerette, C., & de Guerville, F. (2004). *J. Phys.: Condens. Matter*, *16*, S1981.