

Temperature and Liquid Crystal Concentration Effect on Thermal Conductivity of Poly(styrene) Dispersed 5CB Liquid Crystal

Abderrahim Boudenne,¹ Smaïn Khaldi²

¹CERTES, IUT de Créteil, Université Paris-12, Val de Marne, 61 Avenue du Général De Gaulle, 94010 Créteil, France

²LPP, Institut de Physique, Université Abou-Bakr Belkaid, BP 119, 13000 Tlemcen, Algérie

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ABSTRACT: In the present work, we study the thermal behavior of Polymer (Polystyrene) dispersed (4-cyano-4'-pentybiphenyl) 5CB liquid crystal film composite. A photopyroelectric device was used to study thermal conductivity at homeotropic and planar aligned of 4-cyano-4'-pentybiphenyl (5CB) liquid crystal. Thermal conductivity of polystyrene (PS) has been determined and calculated from experimental applied data reported in the literature. Thermal conductivity characteristics of the PDLC films were investigated with three prediction models as a function of

both temperature and liquid crystal concentration in the polymer matrix. We particularly show the behavior of this thermal conductivity in the ON and OFF state. It was found that the difference in the film thermal conductivity ranges between 3 and 21%, depending on the ON and OFF state and the liquid crystal volume concentration. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 481–486, 2003

Key words: thermal properties; PDLC; polystyrene

INTRODUCTION

During the last 10 years, a new class of composite materials has appeared. These materials are called polymer-dispersed liquid crystals (PDLC). They are currently used in several electro-optical applications such as switchable windows,¹ high-definition projection systems, large flat-panel displays, and light shutters for optical signal processing.² In a typical application, a thin PDLC film (about 100 microns thick) is inserted between clear plastic covers.³ The plastic substrates are coated with a very thin layer of a conducting material known as indium tin oxide (ITO). Polymer-dispersed liquid crystals can be prepared in several different ways including encapsulation⁴ and phase-separation processing.⁵ The latter process has become the first manufacturing method. Each method produces PDLC with different properties and characteristics. There are many factors influencing the properties of the PDLC material among, which (a) the polymer and liquid crystal types that are used; (b) the cooling and heating rates in the production; (c) the size (0.01 to 40 microns) and morphology (shape) of the droplets.

The light transmission through a PDLC window depends on the scattering of the droplets and the difference between the droplet refractive index and their polymer matrix. When a voltage is applied, however, the refractive index of the individual droplets aligns with the field. These generate a difference between the refractive the index for neighboring droplets and the matrix, and the window appears transparent. In the field OFF, the random array of droplet orientation provides significant differences in indices and hence strong scattering. In this state, the window diffuses the light. The choice of the polymer and the liquid crystal refractive index has been the object of several research works^{6,7} to improve the light PDLC film transmission. Research works on the heat transfer and specially on thermal conductivity in polymers and polymer composites have increased in recent years.^{8–10} In the present work, we are interested in the theoretical study of thermal conductivity of the PDLC film using thermal conductivity models of the composite materials.

THEORETICAL MODELS

The importance of thermal conductivity in polymers and polymer composites has increased in recent years due to the need for appreciable levels of thermal conductance in circuit boards, heat exchangers, and machinery. It is also important to know thermal conductivity of filled compositions to model the heat transfer

Correspondence to: A. Boudenne (boudenne@univ-paris12.fr).

process. There have been many theoretical models describing thermal conductivity of two phases mixture, particularly filled composites of heterogeneous polymers.

In this study, we use three different prediction models. We assume that our system is at a thermal local equilibrium. This implies that the difference of thermal conductivity as well as the contact resistance between the matrix and the droplet is weak. Subsequently, our studied system in this work will be associated to the homogeneous one. The rule of mixtures is a first-order bound, which assumes a uniform state of temperature gradient across both phases and a uniform state of heat flux through the entire material. This model treats each component as contributing to the thermal conductivity of the composite in an amount equal to the volume fraction of each component. This approach is simply assimilated to a series model based on the analogy of electrical current flow in a series circuit. The basic equation is given by:

$$\frac{k_{\text{eff}}}{k_2} = (1 - \phi_1) + \frac{k_1\phi_1}{k_2} \quad (1)$$

where, k_{eff} , k_1 , k_2 are, respectively, the thermal conductivity of the composite, of the polymer matrix, and of the filler. ϕ_1 represent the filler volume fraction.

The Hatta and Taya model was referred to the second-order bounds model.¹¹ It takes into account the filler geometry, as well as the perturbation between the matrix and the filler. This thermal conductivity model was developed with the analogy of the short fiber modulus at different orientation. The solution of the Hatta and Taya model for the spherical inclusion was given by:

$$\frac{k_{\text{eff}}}{k_2} = 1 + \frac{\phi_2}{\frac{(1 - \phi_2)}{3} + \left(\frac{k_1}{k_2 - k_1}\right)} \quad (2)$$

where ϕ_2 is the matrix volume fraction.

The third and last one is the Torquato¹² model (third- and fourth-order bounds). According to this model, the mechanism of heat transfer is far different from the electrical transport. For this model, microstructural parameters are derived using a set of statistical functions. This model is the same as the second-order bounds but takes into account a parameter of statistical perturbation around each filler particle. This approach is appropriate to a dispersed phase of spherical or cylinder particles. In the spherical case, the Torquato model is given by:

$$\frac{k_{\text{eff}}}{k_2} = \frac{1 + \phi_1\beta_{12} - \phi_2\xi_1\beta_{12}^2}{1 - \phi_1\beta_{12} - \phi_2\xi_1\beta_{12}^2} \quad (3)$$

with

$$\beta_{12} = \frac{k_1 - k_2}{k_1 + (d - 1)k_2} \quad (4)$$

where d is the constant for the dimension of the system ($d = 3$ for the sphere particles) and ξ_1 is the microstructural three-point parameter.¹³ The value of ξ_1 lies in the range of $0 \ll \xi_1 \ll 1$ is tabulated in Table I at selected values of ϕ_1 for symmetric cell materials with spherical cells of the same size for fully penetrable and impenetrable spheres.¹³

EXPERIMENTAL SETUP MEASUREMENT

The thermophysical parameters of the pure liquid crystal have been determined in collaboration with the Photothermal Research Group Laboratory at the University of Rome.¹⁴ The photopyroelectric setup has been used to determine the thermal conductivity of homeotropic and planar alignment of 4-cyano-4'-pentylbiphenyl (5CB) liquid crystal, as a function of temperature. This method permits to make a measurement of the thermal conductivity for different orientation of the droplet configuration. The surface of the blade underwent a treatment (Fig. 1) to get an optimum alignment of the liquid crystal for the two profiles (homeotropic or planar alignment at the heat propagation axis). The 5CB liquid crystal sample is sandwiched between a glass plate and a pyroelectric transducer. The surface has been periodically heated and the temperature oscillation has been introduced at the opposite surface and detected by the transducer. For that, we need to introduce a small temperature gradient in the sample to obtain a good signal to noise ratio, thus allowing a high temperature resolution in the determination of the thermal parameters.¹⁵ The amplitude and the phase of pyroelectric signal, which depend on the sample thermophysical parameters, are analyzed and amplified. The transducer of a 300- μm thickness is in LiTaO_3 , and the liquid crystal sample

TABLE I
Values of the Three-Point Parameter ξ_1 for the Spherical Inclusion

| Filler volume fraction ϕ_1 | Fully penetrable spheres | Random impenetrable spheres |
|---------------------------------|--------------------------|-----------------------------|
| 0.10 | 0.056 | 0.021 |
| 0.20 | 0.114 | 0.040 |
| 0.30 | 0.171 | 0.059 |
| 0.40 | 0.230 | 0.084 |
| 0.50 | 0.290 | 0.141 |
| 0.60 | 0.351 | 0.328 |
| 0.65 | — | — |
| 0.70 | 0.415 | — |

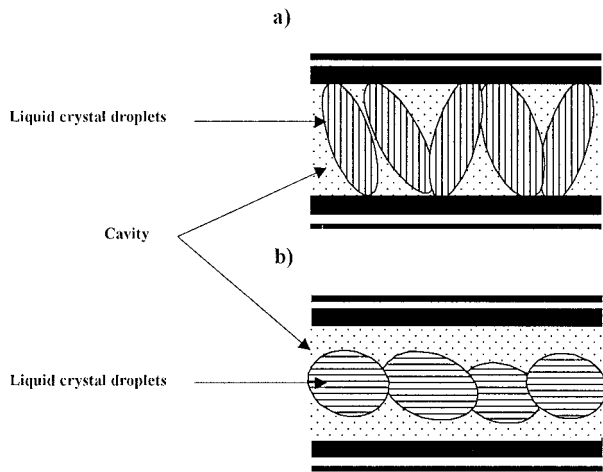


Figure 1 Droplets orientation in homeotropic alignment (a) and planar alignment (b).

thickness is about 30 μm . The heat source is a He-Ne laser-type modulated in the frequency absorbed by the metallic plate. The sample and the transducer were contained in a vat, and the measurements were realized every minute with a temperature variation stage.

RESULTS AND DISCUSSION

The 5CB liquid crystal case

Figure 2 shows thermal conductivity for 5CB liquid crystal samples with homeotropic and planar alignments (k_{\parallel} and k_{\perp}) in the temperature range of 22 to 45°C. Prior to nematic–isotropic transition temperature ($T_{\text{NI}} = 35^{\circ}\text{C}$). The value k_{\parallel} of thermal conductivity decreases from 0.245 to 0.185 W/mK, then falls abruptly close to T_{NI} . After this latter and in the isotropic phase, k_{\parallel} remains fairly constant up to 45°C. In Figure 2, the variation of 5CB liquid crystal thermal conductivity as a function of temperature for a planar alignment k_{\perp} is also represented. We give this configuration to show the evidence effect of the liquid crystal droplets orientation. Contrary to k_{\parallel} , the thermal conductivity values of k_{\perp} increases from 0.12 to 0.13 W/mK, when the temperature rises from 22 to 34°C. Close to T_{NI} , k_{\perp} increases abruptly to 0.15 W/mK. In the isotropic phase, the two data sets (k_{\perp} and k_{\parallel}) coincide; the values remain constant from the nematic–isotropic transition temperature up to 45°C.

To get a thermal conductivity variation as a function of temperature in the absence of alignment (disorder alignment), we consider a conventional model used for the geometric configuration of some scattering droplets with a thickness of a few microns. This model is also used in the electro-optical domain, and more precisely in the calculation of PDLC film refractive index in the OFF state. In fact, the liquid crystal re-

fractive indices variation is the same as that of the thermal conductivity variation. We can assume in the absence of alignment that:

$$k_{\text{AA}} = \frac{1}{3}(k_{\parallel} + 2k_{\perp}) \quad (5)$$

where, k_{\parallel} , k_{\perp} , and k_{AA} are, respectively, the thermal conductivity of liquid crystal in homeotropic alignment, in planar alignments, and in the absence of alignments.

The variation of k_{AA} is also illustrated in Figure 2. We note that above T_{NI} , the thermal conductivity k_{AA} changes slightly from 0.16 to 0.15 W/mK. After the critical point T_{NI} , k_{AA} remains constant at a value of 0.15 W/mK.

The polymer matrix case

Also in Figure 2 the thermal conductivity variation of the polystyrene as a function of temperature is represented. These results have been fitted to experimental data above the glass transition temperature,¹⁶ T_g . In this figure and for this PDLC composite film temperature utilization, we note that the thermal conductivity k_{PS} of the polystyrene increases as a function of temperature. The data for thermal conductivity of polystyrene have been extrapolated in this interval of temperature (22 to 47°C) to the expression:

$$k_{\text{PS}} = 0.105 + 2.2 \cdot 10^{-4} T \quad (6)$$

where, k_{PS} is the thermal conductivity of Polystyrene, and T is the temperature.

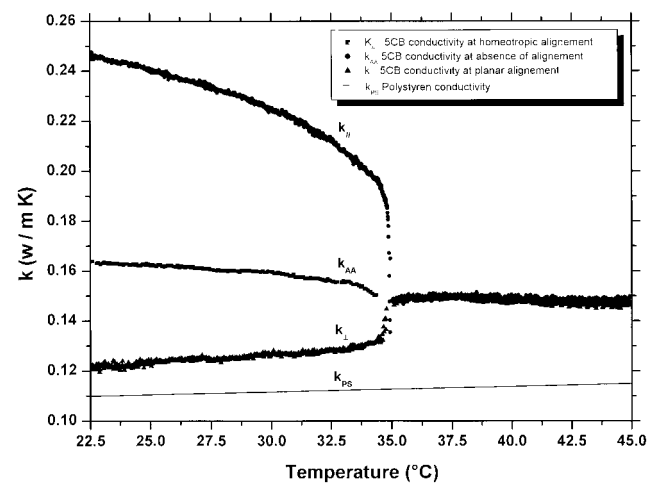


Figure 2 Liquid crystal (5CB) and polystyrene thermal conductivity variation vs. temperature.

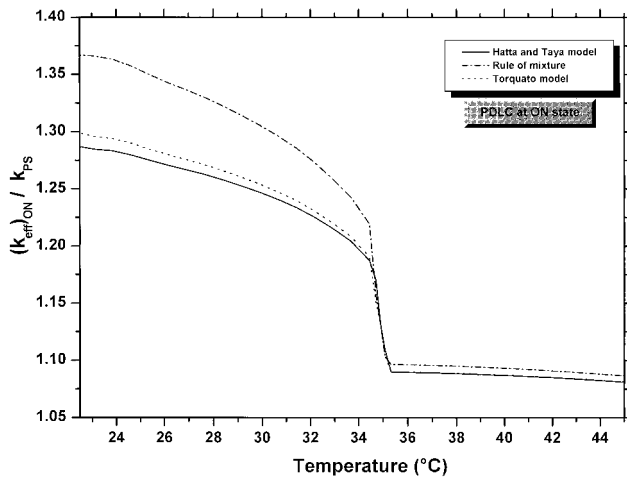


Figure 3 Thermal conductivity variation of PDLC (70% PS and 30% 5CB) at the ON state vs. temperature.

The polymer dispersed liquid crystal (PDLC) case

To determine the thermal conductivity behavior of this PDLC film composite, we use three different prediction models as function of both temperature and liquid crystal concentration in the polymer matrix. We show particularly with these models, the thermal conductivity composite film behavior at the opaque and transparent states. In eqs. (1) to (3), k_{eff} can be replaced by $(k_{\text{eff}})_{\text{ON}}$ when the film is at ON state and $(k_{\text{eff}})_{\text{OFF}}$ at the OFF state.

The ON state

To simulate the PDLC film at the transparent state and where the liquid crystal droplets are oriented in the direction of the field, we take k_{\parallel} as the liquid crystal value of the thermal conductivity in this state and k_{PS} as the polystyrene thermal conductivity. Figure 3 shows the temperature dependence of the ratio $(k_{\text{eff}})_{\text{ON}}/k_{\text{PS}}$ PDLC film (70%PS and 30%5CB) at the ON state. For temperature from 22 to 45°C, we note that the first-order bound model (rule of mixture) gives slightly lower values than the Hatta and Taya model (second-order bound), and Torquato model (third- and fourth-order bound). These last (Torquato model) give the same values for interpenetrating and nonpenetrating dispersed phase. Before the liquid crystal droplet temperature transition, which are anchoring in the polymer matrix, both Hatta and Taya, and Torquato models give very near values. After the liquid crystal T_{NI} , the thermal conductivity of the PDLC film stays constant for this temperature variation. We note also that values given by the first-order bound model are slightly higher than the ones obtained by the two other models.

To see the effect of liquid crystal concentration in the thermal behavior of PDLC film, we use the same models of prediction at room temperature ($T = 25^\circ\text{C}$). However, we vary the volume concentration of 5CB in the mixture from low (<10%), through medium (10–30%), to high (30–60%). Figure 4 shows the variation of the PDLC film (5CB/PS) thermal conductivity at 25°C as a function of 5CB volume in the ON state. In this figure, we note that when the concentration of the liquid crystal increases, the thermal conductivity of the PDLC film at the ON state increases also. The values obtained by the both Hatta and Taya and Torquato models are almost close to one another for different concentrations. The first-order bound model shows good agreement with second-order bound, third- and fourth-order bound at 5CB low volume, but give lower values than other models when the liquid crystal concentration increases.

The OFF state

To get thermal conductivity of the PDLC film at the OFF state, it will be necessary to take the thermal conductivity values of liquid crystal (k_{AA}) at this state, k_{AA} being the value of 5CB in the absence of alignment. Figure 5 shows the variation of the ratio $(k_{\text{eff}})_{\text{OFF}}/k_{\text{PS}}$ as a function of the temperature of the PDLC film (70%PS and 30%5CB) at the OFF state. We note from the ratio $(k_{\text{eff}})_{\text{OFF}}/k_{\text{PS}}$ that the PDLC composite film thermal effective conductivity value $(k_{\text{eff}})_{\text{OFF}}$ is almost the same in the two state of liquid crystal phases. The first-order bound model gives higher values than those of Hatta and Taya and Torquato models. These last models are perfectly in agreement for low, medium, and high volume concentration.

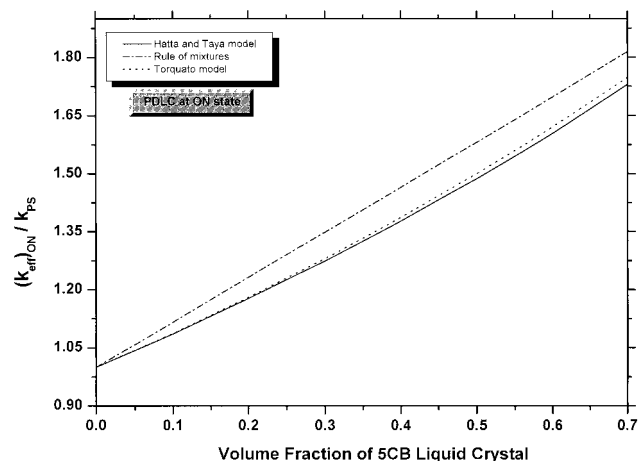


Figure 4 Thermal conductivity of PDLC (PS/5CB) variation in the ON state at 25°C vs. 5CB volume fraction.

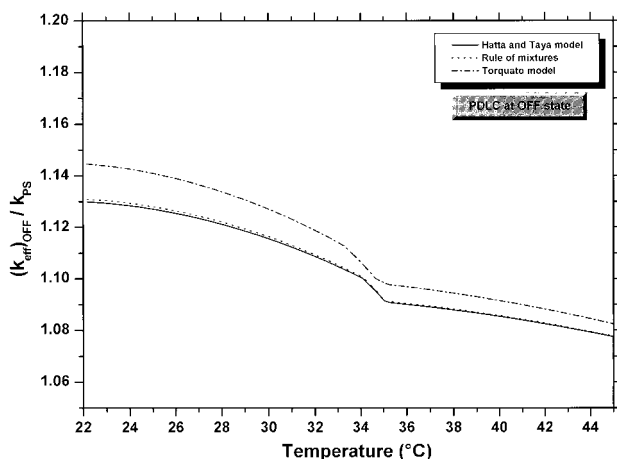


Figure 5 Thermal conductivity variation of PDLC (70% PS and 30% 5CB) at the OFF state vs. temperature.

The thermal conductivity values of the same PDLC film at room temperature (25°C) in the OFF state are also shown in Figure 6 as a function of 5CB volume fraction of polymer matrix. At the OFF state the two models, Hatta and Taya and Torquato models, give the same values for different concentrations. The rule of mixtures gives higher values than the two other models when the concentration of liquid crystal increases. We can say, after analysis of these two last figures that the thermal conductivity values $(k_{\text{eff}})_{\text{ON}}$ and $(k_{\text{eff}})_{\text{OFF}}$ of this PDLC film (70%PS and 30%5CB) in the two states, ON and OFF increase respectively as a function of 5CB liquid crystal concentration in the mixture.

Discussion

The PDLC film thermal conductivity value variation for the three models is different both before and after liquid crystal nematic-isotropic temperature transition. This can be explained because in the nematic phase, the orientation of the liquid crystal droplets anchoring in the polymer matrix influence a thermal conductivity behavior of the PDLC film. Do to the fact of applying a field, the liquid crystal droplets can be oriented in only field direction. This alignment generates some free space between rows in the liquid crystal droplets and makes possible a better heat propagation. When the temperature increases, the droplets expand, distort, and take progressively a precedent free space. This progressive reduction of the free space involves an increase in the thermal resistance, which obstruct the heat good propagation. However; for the OFF state and when the liquid crystal anchoring in the polymer matrix was at nematic phase, the liquid crystal droplets distort as a function of an increase temperature. This variation is not as significant as the one in the ON

state. Nevertheless, it generates a reduction of thermal resistance. Consequently, it facilitates the heat propagation in the PDLC, and demonstrates an increase in thermal conductivity. After the liquid crystal T_{NI} , the droplets anchoring in the polymer matrix shift to the isotropic phase where in this configuration they have no preferential direction, and thermal conductivity becomes and remains constant in the ON and OFF states. The increase in thermal conductivity of the composite film at the ON and OFF state as a function of liquid crystal concentration is foreseeable.

CONCLUSION

This article presents the results of a theoretical study of the thermal behavior of (PS/5CB) composite film. The thermal conductivity characteristics of the PDLC (PS/5CB) films were investigated with three prediction models as a function of temperature and liquid crystal concentration in the polymer matrix at the ON and OFF states.

We have noted that the thermal conductivity temperature depends on the temperature and molecule alignment of pure liquid crystal in PDLC composite. The efficient thermal conductivity values of the composite film given by second-order bound are in agreement with the ones of the third- and fourth-order bound will give the same values in the penetrable and impenetrable liquid crystal droplets case. Nevertheless, we note that the second order bound can be taken as a prediction model based on the thermal behavior of anisotropic composite materials. In the end, we can say also that the concentration of the liquid crystal 5CB volume can produce a difference of 3 to 21% of the PDLC film thermal conductivity between the ON and the OFF states.

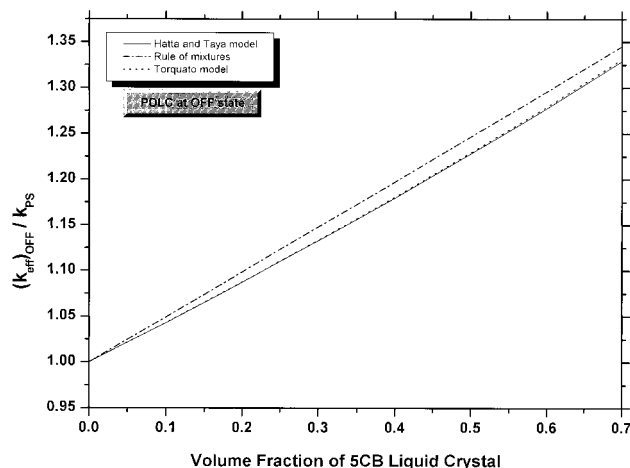


Figure 6 Thermal conductivity of PDLC (PS/5CB) variation in the OFF state at 25°C vs. 5CB volume fraction.

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