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Citation for published version (APA):

Boxtel, van, M. C. W., Janssen, R. H. C., Bastiaansen, C. W. M., & Broer, D. J. (2001). Viscoelastic liquid crystal colloids for the continuous processing of twisted nematic electro-optical cells. *Journal of Applied Physics*, 89(2), 838-842. <https://doi.org/10.1063/1.1335648>

DOI:

[10.1063/1.1335648](https://doi.org/10.1063/1.1335648)

Document status and date:

Published: 01/01/2001

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
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Viscoelastic liquid crystal colloids for the continuous processing of twisted nematic electro-optical cells

Marysia C. W. van Boxtel^{a)}

Department of Chemical Engineering, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

Rob H. C. Janssen and Cees W. M. Bastiaansen

Department of Chemical Engineering, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands and Department of Materials, ETH-Zentrum UNO C15, CH-8092 Zürich, Switzerland

Dick J. Broer

Department of Chemical Engineering, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven and Philips Research Laboratories, Prof. Holstlaan 4, 5656 AA Eindhoven, The Netherlands

(Received 14 April 2000; accepted for publication 1 November 2000)

Liquid crystal colloid materials are described based on the liquid crystal (LC) E7 and submicron sized poly(methyl methacrylate-*co*-divinylbenzene) particles. Application of a thermal treatment to the composite material produces a finely dispersed network of the internally crosslinked polymeric inclusions in the LC-E7. Dynamic rheological measurements on the LC colloids show that the presence of this network imposes pronounced viscoelastic behavior on the material, which may be exploited in the manufacturing of large-area twisted nematic (TN) electro-optical cells via continuous methods as an alternative to the currently available batchwise routes. The electro-optical characteristics of TN cells based on the composite material are approximately comparable to the electro-optical characteristics of a reference cell filled with pure LC E7, which ensures that the largely increased viscoelasticity of the composite does not lead to a degradation of electro-optical properties. © 2001 American Institute of Physics. [DOI: 10.1063/1.1335648]

I. INTRODUCTION

Twisted nematic electro-optical cells, introduced in the early 1970s,¹⁻³ employ electrical addressing to orient a low molecular weight liquid crystal (LC) layer from a 90° twisted state throughout the thickness of the cell into a homeotropically aligned state and vice versa. The contrast between the off and the on state is visualized by the use of crossed polarizers that ensure the 90° twisted state to be the transparent off state and the homeotropic state to be the light-blocking, dark on state. Advantages of the twisted nematic (TN) configuration are its intrinsically low switching voltages and fast switching kinetics. However, because the pure LC is lacking in rheological and mechanical stability, the present display-cell technology requires a complex batchwise cell construction process in combination with a capillary filling step. This, in fact, makes the manufacturing of TN cells very laborious and expensive and limits the application of these TNs merely to relatively small areas.

To overcome the difficulties mentioned above, in previous articles we have reported on the use of mechanically stable composite materials for *scattering-type* electro-optical switches, based on a random dispersion of polymeric particles in LC,⁴ on dendrimer-stabilized LC phases,^{5,6} and on thermoreversible organogels.⁷ The specific viscoelastic prop-

erties of such LC composites give access to continuous display production processes, such as web coating on plastic substrates. The quasisolid behavior at zero flow allows perfect thickness control, even at nonhorizontal substrates, and easy lamination or coating of covering layers. However, whereas the macroscopic behavior is solid-like, the rotational mobility on molecular scale is maintained, thus preserving the high electro-optical switching rates.

Recently, we also investigated the use of the organogelator 12-hydroxyoctadecanoic acid (HOA)⁸ in the liquid-crystal LC-TL213 to generate a mechanically stable *TN-castable* material, again with the objective of developing materials suitable for continuous display production routes. It was shown that the addition of a small amount ($\ll 1\%$) of HOA resulted in highly elastic gel-like materials that could be casted into monolithic structures, e.g., of TN type. Contrast ratios and switching times of the TN cells based on these gels were largely unaffected when compared to the properties of conventional cells, thus ensuring that the largely increased material elasticity does not lead to a deterioration of electro-optical activity of the LC gel.

In this article, we report on the use of LC colloid materials to create monolithic structures with increased mechanical stability (when compared to neat LC), of use in continuous processing routes for TN displays. The prime motivation for using LC colloids, as an alternative to the thermoreversible gel concept, was to reduce switching voltages, while preserving the excellent mechanical properties that were ob-

^{a)}Author to whom correspondence should be addressed; electronic mail: M.v.Boxtel@tue.nl

tained earlier with thermoreversible gels.⁸ Thus, here the attention will be focused on employing the formation of the network-type aggregates by the polymeric spherical inclusions in the production of a TN-type electro-optical switch (the network formation process itself has recently been described for lyotropic and thermotropic LC materials in, respectively, Refs. 9–11 and 12). Furthermore, we evaluate the mechanical and electro-optical properties of the LC colloids, as used in electro-optical cells with TN configuration.

II. EXPERIMENT

A. Materials

The LC material used was LC E7 ($T_{N-I}=60\text{ }^{\circ}\text{C}$, $\epsilon_{\perp}=5.2$, and $\epsilon_{\parallel}=19$, $\Delta n=0.2246$), a four-component LC mixture of cyanobiphenyls and a cyanoterphenyl purchased from Merck Ltd (where T_{N-I} is the nematic–isotropic transition temperature).

The polymeric filler particles used in this study were prepared via dispersion polymerization of methyl methacrylate and divinylbenzene in *n*-heptane, as described previously.⁴ In order to obtain a highly black on state and a reduced light scattering in the transparent off state, the refractive index of the particles was matched to the ordinary refractive index of LC-E7. This was done by starting the synthesis from the proper monomer ratio, as calculated from the Lorentz–Lorenz equation.¹³

B. Characterization methods

The morphology of the LC colloids in TN cells was examined at temperatures ranging from room temperature to $150\text{ }^{\circ}\text{C}$ with the aid of a Zeiss Universal high resolution optical microscope equipped with a Linkam TMS 92 hot stage.

The rheological properties of the LC colloid materials were measured at $T=26\text{ }^{\circ}\text{C}$ with an ARES Rheometric Scientific Laboratory instrument equipped with 25 mm circular parallel plates. The materials were appropriately placed between the plates at an elevated temperature of $150\text{ }^{\circ}\text{C}$, and subsequently cooled to $26\text{ }^{\circ}\text{C}$. During cooling, the registered normal force, exerted on the upper plate, was kept constant by carefully readjusting the distance between the plates. Finally, the dynamic rheological properties of the approximately 0.5 mm thick films were determined after it was observed that the normal force remained constant in time.

The electro-optical characteristics of TN cells were recorded using a Display Measuring System DMS 703 obtained from Autronic Melchers GmbH. ac voltages of 100 Hz square waves were applied in steps of 0.1 V and with a scanning rate of 1 V s^{-1} . Cells were illuminated with a 100 W halogen light source provided with a diffuser plate. The electro-optical cells were directly placed on the diffuser plate between crossed polarizers. The spot size of the detector was set on 0.2 mm and the sample–detector distance was set in focus before measurement.

C. Cell design

TN cells were prepared with indium–tin–oxide (ITO) coated glass (Merck, type 327 735 PO), cut in pieces of

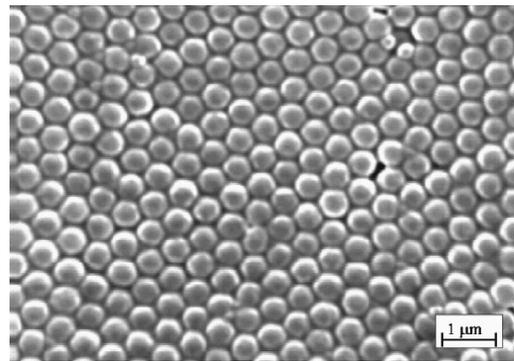


FIG. 1. Scanning electron micrograph of highly monodisperse 630 nm sized refractive index matched poly(methyl methacrylate-*co*-divinylbenzene) particles.

$3.0\times 3.0\text{ cm}$. The glass slides were cleaned in a cleanroom after which a polyimide precursor solution (AL 1051, JSR Electronics) was spincoated (5 s at 1000 rpm, 40 s at 3500 rpm) on top of the plate's ITO side. After preheating for 10 min at $100\text{ }^{\circ}\text{C}$ and 90 min baking at $170\text{ }^{\circ}\text{C}$ under vacuum, the polyimide layers were softly rubbed in one direction with a velvet cloth. On one of the plates, constituting a cell, an ethanol solution containing $6\text{ }\mu\text{m}$ polystyrene spheres was spin coated (45 s at 1000 rpm) to ensure a fixed spacing of the plates. TN cells were assembled by mounting two glass slides, of which one was provided with an UV curable sealant (UVS 91, Norland Products Inc.), on top of each other. Before UV curing, it was verified that glass slides were placed such that the orientation layers on the two substrates were directed mutually perpendicular to each other.

III. RESULTS AND DISCUSSION

Figure 1 shows a scanning electron micrograph of the monodisperse 630 nm polymeric particles synthesized for this study. LC colloids were prepared by ultrasonic mixing of a preset amount of LC-E7 with a preset amount of a dispersion of the polymeric particles in *n*-heptane. After 24 h evaporation of the *n*-heptane from the mixture in a vacuum chamber at room temperature, homogeneously dispersed polymer/LC composite materials, previously termed polymer filled nematics,⁴ with polymer contents of 2.7 and 6.4 wt % were obtained.

Subsequently, TN electro-optical cells of $6.4\text{ }\mu\text{m}$ thickness were filled with the blends by capillary action at $150\text{ }^{\circ}\text{C}$. After filling and cooling to room temperature, optical micrographs of the cells show that the polymeric particles have assembled into a network consisting of ordered interconnected aggregates (Fig. 2).

The origin of this rearrangement phenomenon was studied visually in a polarizing microscope equipped with a hot stage. It was observed that during heating to temperatures around $150\text{ }^{\circ}\text{C}$, due to the increased Brownian motion of the polymeric inclusions at elevated temperatures, the ordered structures were gradually broken down. This eventually led to the formation of homogeneous dispersions of the particles in the isotropic LC that showed no evidence of particle aggregation on length scales accessible by optical microscopy.

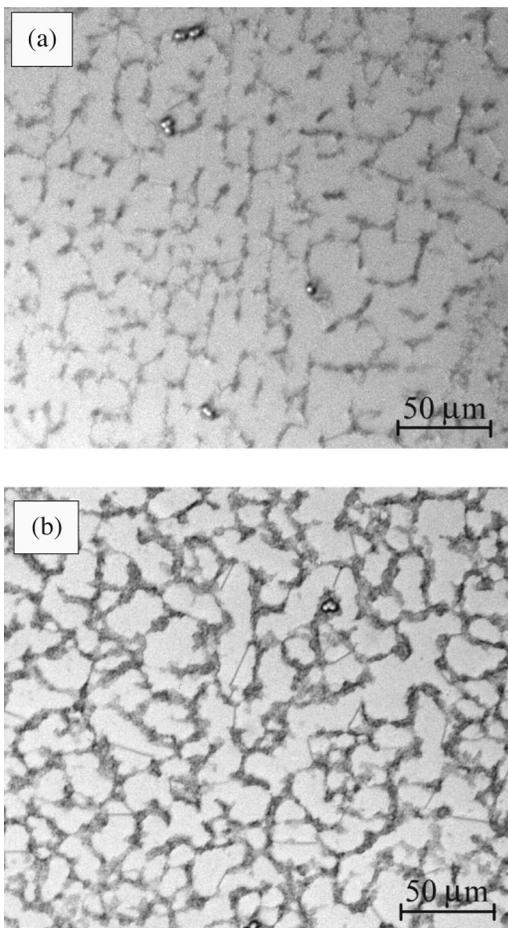


FIG. 2. High resolution optical micrographs of $6.4 \mu\text{m}$ thick TN cells filled at 150°C and subsequently cooled to room temperature at 50 K min^{-1} with: (a) 2.7 wt % and (b) 6.4 wt % polymer/LC blends. [The large spheres visible in (a) are polystyrene spacers.]

After this homogenization of the LC colloids, during cooling to room temperature, it was observed that the inclusions remained nicely dispersed showing no pronounced signs of aggregation all the way down to the nematic–isotropic transition temperature T_{N-I} of LC-E7. It was only upon passing the nematic–isotropic transition temperature that the growing nematic droplets, which appeared to be free of polymeric inclusions, pushed aside the dispersed particles by their expanding interfaces.^{9,12} Therefore, ultimately, the polymeric particles were collected at the disclination lines that form when growing nematic droplets meet, resulting in the formation of the network structure, depicted in Fig. 2. Clearly, the most obvious reason for the polymeric spheres to be expelled from the nematic droplets into the coexisting isotropic fluid is the increase in free energy due to elastic distortion of the nematic director field, which is needed in case dispersion of spheres in a nematic phase occur.^{14–16}

The network formation process turned out to be fully reversible and might be influenced by the speed at which the $N-I$ transition is passed: During slower passage, fewer nuclei are formed, giving the nematic droplets more time to grow, resulting in somewhat larger LC domains and a polymer particle network with a larger mesh size. It should be clear that the network formation process relies on the occur-

rence of a phase separation between the dispersed polymeric phase and the LC phase.

Stability tests were performed in order to study whether the network, formed upon passing the nematic–isotropic transition temperature region, displays a long-term stability or ultimately clusters into macroscopic aggregates. For this purpose, thin tubes with an inner diameter of 2 mm were filled via capillary action with the 2.7 and 6.4 wt % polymer/LC blends at a temperature of 150°C . After cooling to room temperature, the tubes were placed vertically and sedimentation effects were studied over a period of 2 weeks. In both cases, the light scattering remained uniform over the whole length ($l=2 \text{ cm}$) of the tube during the whole investigation period, indicating that the network is stable and able to resist gravitational forces. In another set of experiments, the tubes were placed in an oven at 150°C , directly after the filling process. In case of the 2.7 wt % polymer/LC blend, a macroscopic settling of the polymeric particles could be detected after 20 min and in the case of the 6.4 wt % blend, sedimentation occurred after several hours. Since these sedimentation times exceed the typical time of a few minutes needed to fill a TN cell and cool to room temperature, it is not expected that significant sedimentation occurs during filling and cooling of TN cells. This is in agreement with very recent experiments, in which the three-dimensional extension of the polymeric aggregates has been demonstrated by confocal microscopy for similar systems.¹² Further support for this hypothesis comes from the dynamic mechanical analysis, which established that the presence of the particle network strongly enhances the mechanical stability of $\pm 0.5 \text{ mm}$ thick films of the LC colloid, when compared to neat LC-E7.

This can be seen from Fig. 3(a), which shows that for strains up to 1%, the 2.7 and 6.4 wt % polymer/LC blends both exhibit linear viscoelastic behavior. The plateau values for the elastic storage and loss moduli point to $G'(\gamma)=5.0 \times 10^3 \text{ Pa}$ and $G''(\gamma)=2.5 \times 10^3 \text{ Pa}$ (2.7 wt %) and $G'(\gamma)=8.5 \times 10^4 \text{ Pa}$ and $G''(\gamma)=4.5 \times 10^4 \text{ Pa}$ (6.4 wt %), which are several orders of magnitude higher than in case of neat LC-E7. As shown in Fig. 3(a), at angular frequency $\omega = 1 \text{ rad s}^{-1}$, the LC colloids possess an impressive stiffness of $G' \approx 10^4 \text{ Pa}$, comparable to that of many of the well-known organo gels,¹⁷ and viscosity $\eta = G''/\omega \approx 10^3 \text{ Pa s}$, comparable to that of the commodity polymers at their processing temperature.¹⁸ As depicted in Fig. 3(b), the basic characteristics of the material are maintained over 5 frequency decades. Here, it should be noted that at higher frequencies, the difference between G' and G'' tends to increase, reflecting that the material behaves somewhat stiffer and less viscous at these frequencies.

The data condensed in Fig. 3 are commensurate with the presence of a “dynamic network structure in an LC matrix.” Obviously, upon linear deformation of the composite material, the particle network does exhibit an elastic energy storage. However, the relatively high G'' value points to reorganizations (break and subsequent buildup) within the network, associated with viscous flow. Figure 3(b) points out that at higher frequencies this reorganization effect is somewhat less pronounced, as may be explained by the smaller time span at which a reorganization has to take place at increased

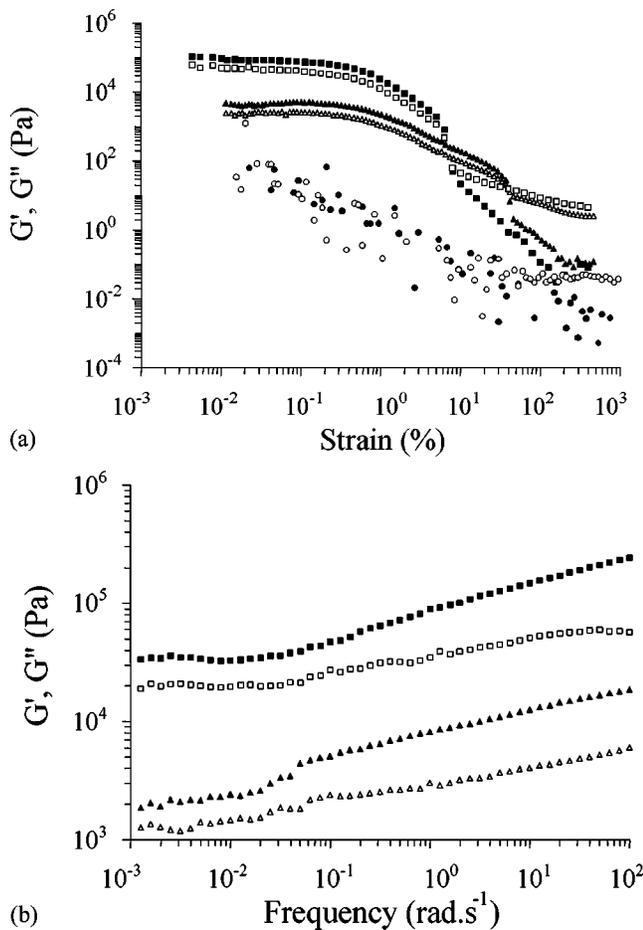


FIG. 3. (a) The elastic storage modulus G' (closed symbols) and loss modulus G'' (open symbols) as a function of the applied strain for the 2.7 wt % (triangles) and 6.4 wt % (squares) polymer/LC blends at angular frequency 1 rad s^{-1} . The G' and G'' values of neat LC-E7 are plotted as a reference (circles). (b) The moduli G' (closed symbols) and G'' (open symbols) for frequencies ranging from 10^{-3} to 10^2 rad s^{-1} at a fixed strain of 0.25% (triangles: 2.7 wt % blend; squares: 6.4 wt % blend).

ω 's. Clearly, the driving force for the dynamic restoration of the network remains to be the gain in absolute free energy that may be obtained if elastic distortions of the nematic director field are avoided.

From an applications point of view, the rheology of the LC colloids improves the coating properties. In fact, the flow behavior resembles that of the wet coatings used in the coating and paint industry. This may be exploited for the fabrication of TN displays via cost-effective coating processes rather than using the present cell technology. Another advantage is the mechanical stability of the formed layers under stress. This enables the manufacturing of all-plastic LC displays, which withstand external stresses and bending forces without changes in the thickness of the active layer and the corresponding optical properties, while molecular order is preserved.

TN cells filled with the 2.7 and 6.4 wt % blends were characterized with respect to their electro-optical performance. The characteristics of a TN cell filled with neat LC-E7 were taken as a reference. In Fig. 4, the absolute transmittance is depicted as a function of the applied voltage. As a reference measurement, the absolute transmittance was

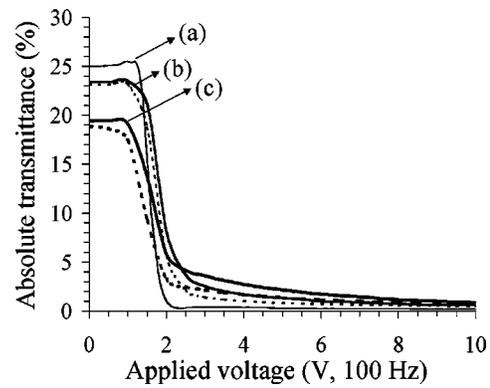


FIG. 4. Transmittance–voltage characteristics for the composite based TN cells and for a LC based TN cell depicted as a function of the applied voltage. (a) LC reference cell: $V_{90}^{up} = 1.87 \text{ V}$; (b) 2.7 wt % blend: $V_{90}^{up} = 2.96 \text{ V}$; (c) 6.4 wt % blend: $V_{90}^{up} = 4.50 \text{ V}$.

measured through the polarizers solely, which were positioned mutually parallel, and it was found to be approximately 26%. From the figure it is seen that the colloidal materials can indeed be reversibly switched from a transparent to a dark state. It should be noted that the absolute transmittance of the transparent state is only slightly affected by the particle network, when compared to cells filled with neat LC-E7. This remarkable result indicates that the particle network, despite its significant effect on the mechanical stability of the composite material, does not prevent the LC matrix from being organized in a twisted fashion by the weak external forces exerted by the polyimide orientation layers when a heating and subsequent cooling stage are applied. A similar observation was previously noted for particle fractal-like aggregates in lyotropic systems by Poulin *et al.*⁹ The relatively high transmittance in the transparent off state and the appearance of a highly black on state also implies that the refractive index matching of the polymeric inclusions and LC matrix is reasonably successful and is not a cause of significant light scattering. Moreover, the particle aggregates only slightly increase the threshold voltages needed for operating the cell, i.e., the switching voltages are very low when compared to conventional dielectric composite systems

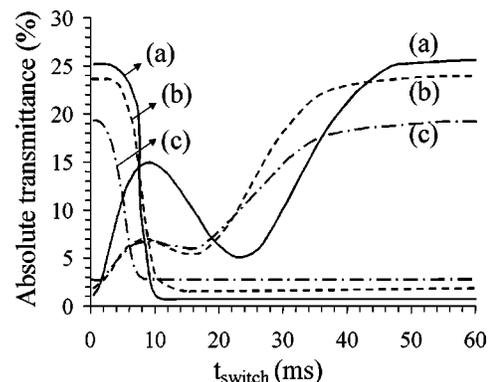


FIG. 5. Rise and decay times for the composite based TN cells and for a LC based TN cell for an applied voltage of 5 V. (a) LC reference cell: $t_{90}^{on} = 8.7 \text{ ms}$, $t_{90}^{off} = 41.2 \text{ ms}$; (b) 2.7 wt % blend: $t_{90}^{on} = 10.0 \text{ ms}$, $t_{90}^{off} = 33.8 \text{ ms}$; (c) 6.4 wt % blend: $t_{90}^{on} = 6.5 \text{ ms}$, $t_{90}^{off} = 37.9 \text{ ms}$.

such as polymer dispersed liquid crystals,^{19–21} silica filled nematics,^{22–24} and thermo-reversible LC gels.^{7,8} In spite of this, their presence does create a transmission “tail” (see Fig. 5), decreasing the steepness of the T – V curve at intermediate switching voltages. Polarized optical microscopy was used to verify that this contrast degradation is caused by the fact that LC molecules in the vicinity of the polymer aggregates reorient into the homeotropic state at somewhat higher voltages. This indeed causes the slight light leaks (transmission tail) in the intermediate voltage regime. The rise and decay times of the TN cells were monitored at an applied voltage of 5 V (Fig. 5). The figure demonstrates that the switching times of the composite based TN cells are comparable to the switching characteristics of the reference cell. It is also perceived that the backflow effects are less pronounced for the electro-optical cells filled with the composite material, which is presumably the direct result of the presence of the polymeric network, which prevents macroscopic flow within the electro-optical cell.

IV. CONCLUSIONS

It was established that LC-E7 filled with monodisperse 630 nm sized poly(methyl methacrylate-*co*-divinylbenzene) particles can be homogenized in the isotropic phase at temperatures around 150 °C. During subsequent cooling and passage of the nematic–isotropic transition temperature T_{N-I} , polymeric aggregates interconnect to form a network structure within the LC matrix. Dynamic rheological measurements on these composites with particle networks indicate that the materials exhibit viscoelastic behavior over the entire frequency range tested, resulting in a strongly enhanced mechanical stability when compared to neat LC-E7, even for inclusion weight fractions as low as 3 wt%. Since, at the same time, the electro-optical characteristics of the LC colloids were shown to be comparable to the characteristics of neat LC phases (and improved with respect to the electro-optical properties of the TN-*castable* thermoreversible gels⁸), the viscoelastic materials are promising with regard to application in continuous manufacturing lines for TN cells as an alternative to the commonly employed batch-type routes.

ACKNOWLEDGMENT

The authors gratefully acknowledge The Dutch Foundation for Applied Sciences (Stichting Toegepaste Wetenschappen, STW) for financial support.

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