

Review

# Advancements in The Cross-Linking and Morphology of Liquid Crystals

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**Abstract:** The liquid crystal state (LC) in polymer chemistry is a topic discussed in varied materials research. The anisotropic properties typical of these compounds are mostly the result of the presence of mesogens in the structure of liquid crystals. This article traces the development of liquid crystal science, focusing on liquid crystal epoxy resins (LCERs) and emphasizing the crucial role of mesogens and their diverse effect on the materials. It also highlights the importance of understanding the morphology of LC polymers, explaining their profound impact on material properties and performance. It explores the cross-linking process of liquid crystal resins and composites, describing how changes in structural factors affect material structure. The article also provides information about hardeners and their influence on the cross-linked structure. Various nanofillers were also discussed, elucidating their impact on the resulting composites.

**Keywords:** liquid crystal; liquid crystal epoxy resin; epoxy resin; hardener; cross-linking; epoxy composite; nanofiller



**Citation:** Zając, W.; Kisiel, M.; Mossety-Leszczak, B. Advancements in The Cross-Linking and Morphology of Liquid Crystals. *Crystals* **2024**, *14*, 440. <https://doi.org/10.3390/cryst14050440>

Academic Editor: Vladimir Chigrinov

Received: 23 April 2024

Revised: 2 May 2024

Accepted: 3 May 2024

Published: 5 May 2024



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## 1. Introduction

The research on liquid crystals traces its origins to the turn of the 19th and 20th centuries. The discovery of liquid crystallinity, made accidentally by the Austrian botanist Friedrich Reinitzer during experiments on cholesterol benzoate, sparked a wave of research that transcended the boundaries of chemistry, merging several scientific disciplines. The introduction of the concept of phases in which a liquid crystal can exist was an important moment in the history of these compounds. Their division, presented in 1922 by Fiedel, distinguishing the phases smectic, nematic, and cholesterol, is used with minor changes to this day. Materials containing liquid crystals in their structure began to be introduced into the industry in the 1960s. The beginnings of their applications were related to optics, and more precisely, to the invention of LCDs. It is having its impact on modern times because in popular opinion liquid crystallinity is still associated with elements of modern electronics. This should not be surprising as currently compounds of this kind are often used in cell phone matrices and computer monitors. Improving parameters for this type of device is constantly a subject of study. Researchers try to improve various aspects, ranging from display color accuracy to information processing speed, and even the responsiveness of touch interfaces. The variety of applications of liquid crystal compounds is not limited solely to optics. Recent studies such as those presented by Zheng et al. [1] show how microscopic LC optical anisotropy engineering can be combined for active optical and photonic applications. Modern research allows for the introduction of a wide range of applications of liquid crystal materials into everyday life [2–4]. One of the division branches of these materials is a category of compounds that can be hardened and cross-linked at various temperatures, thus providing the possibility of controlling their properties thermally. Composites and nanocomposites of liquid crystals have also gained popularity,

as their appearance in recent studies shows an increasing myriad of properties, depending on the selection of the appropriate filler.

This work presents trends in liquid crystal research with an emphasis on liquid crystal epoxy resins. Research on LCs relating their structure to final properties was analyzed. The focus was on the analysis of amine hardeners for liquid crystal epoxy networks and on the analysis of the influence of various fillers on the final properties of the composites. The article presents the development in the following sections: liquid crystals, Liquid Crystal Epoxies, Application Of Liquid Crystal Polymers and liquid crystal epoxy composites.

## 2. Liquid Crystals

Recent years have brought a great variety of research on liquid crystals. These compounds are a class of materials that self-organize to a large extent, exhibiting anisotropic properties and a variety of ordered structures. An important part of the structure of a liquid crystal compound is the mesogenic core. It is a rigid structural element to which liquid crystals owe their properties. Mesogens usually consist of several aromatic rings, providing both the rigidity of the molecule's core and the ability to manipulate its more flexible elements. Their arrangement generally gives the effect of a rod-like or disc-like shape [5,6]. The rings are usually connected by carbon, ether, or ester bonds [7,8]. Scientific publications also describe other types of connections, such as siloxane chains [9] and imine bonds [10]. Individual types of mesogen arrangements are called mesophases and are defined by specific temperature values, which in practice constitute the basis for the applications of these materials. The most recognizable are the nematic and smectic phases. Nematic liquid crystals are used as elements in electronic displays due to their sensitivity to external stimuli, especially electric fields. Other liquid crystal nanostructures, such as smectic, columnar, and cubic phases, are used where their specific arrangement of mesogens is required by materials with specific functions [11].

The study concentrating on liquid crystals is divided into two main trends, describing the type of material they focus on. The first of them is liquid crystal elastomers, which are characterized by long, often interwoven polymer chains, which make them highly elastic. These materials are the subject of many studies due to their flexibility, which results in a wide range of applications including soft robotics, and the production of sensors and actuators [12–14]. Problematic, however, is the fact that the arrangement of mesogens in elastomers must be established before the cross-linking reaction stops the molecular movement, as well as the fact that they cannot be processed or recycled like thermoplastics due to the permanent covalently cross-linked network [15].

The second direction of research is thermosetting liquid crystals. Even ordinary thermosetting resins are considered key polymer materials, playing an important role in various application areas, such as the synthesizing of coatings, the production of packaging for electronics and adhesives, and the production of aerospace composites. Their importance results mainly from exceptional mechanical strength, resistance to chemical agents, and high temperature, as well as dimensional stability [16–18]. Thermosetting liquid crystal resins combine the advantages mentioned above with the possibilities offered by the presence of mesogenic cores in the molecular structure of their molecules [19].

## 3. Liquid Crystal Epoxies

Currently, the main topic of study across multiple research centers revolves around the synthesis and modifications of liquid crystal epoxy resins (LCER). These promising materials are an ideal example to illustrate the progress taking place in the field of liquid crystals [19]. They constitute an important class of thermosetting polymers, characterized by rod-like mesogenic structures, flexible connecting fragments—spacers—and epoxy groups usually located at the ends of the monomer molecule [8,20,21]. An example structure of LC epoxy molecule is shown in Figure 1.



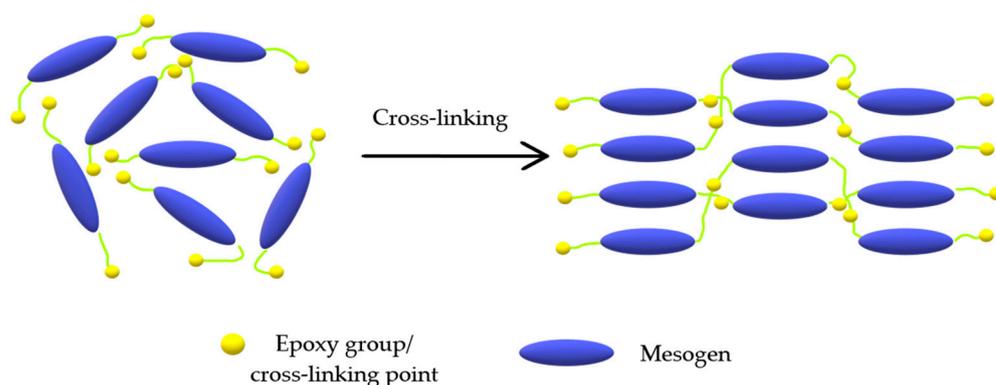
Due to the potential of the above factors, research on liquid crystal monomers also includes innovative syntheses that result in compounds containing long spacers in their structure. One of the examples is the liquid crystalline epoxy monomer which takes the form of the letter Y and has long, flexible chains and mesogenic cores with a high aspect ratio [28]. Research on these topics is aimed at constantly improving the mechanical properties of the hardened product.

Generally, the features of a liquid crystal molecule are affected by all the elements of its structure. Such a compound must not have a volume that is too small for mesogenic elements to exist in it. It also should not be very big, both in terms of volume and molecular weight. A large steric hindrance resulting from the structure of the molecule may lead to the weakening of  $\pi$ - $\pi$  bonds, adversely affecting the close ordering of mesogens, which in turn results in a weakening of the properties of the final material, such as thermal conductivity [29].

The characteristics of liquid crystal epoxy resins might be negatively affected by the ability of the molecule to rotate. As mentioned earlier variations in mesogen junctions, may exhibit differing tendencies for such movements. While the inclusion of siloxane chains enhances the material's hardness in comparison to aliphatic chains, they tend to rotate freely, thereby reducing their thermal properties. Addressing this issue, Harada et al. in the publication [30] propose a solution consisting of introducing cyclic tetrasiloxane integrated with four liquid crystal epoxy structures. This resulted in the formation of a larger molecule in which free rotation was stopped and the melting point was lowered. Additionally, the cyclic structure's compatibility with the polymer network enhances the material's cross-linking degree.

### 3.2. Liquid Crystal Epoxy Networks

The process of creating liquid crystal epoxy networks (LCEN) involves the controlled hardening of epoxy resin in the presence of catalysts and hardeners. During this process, the epoxy and hardener molecules react with each other, creating a durable, three-dimensional polymer network that surrounds and bonds the liquid crystal domains together. In other words, the curing reaction induces cross-linking, thereby increasing microcrystallinity and facilitating heat transfer in the polymer matrix [25,31]. The cross-linking process is pictured in Figure 3.



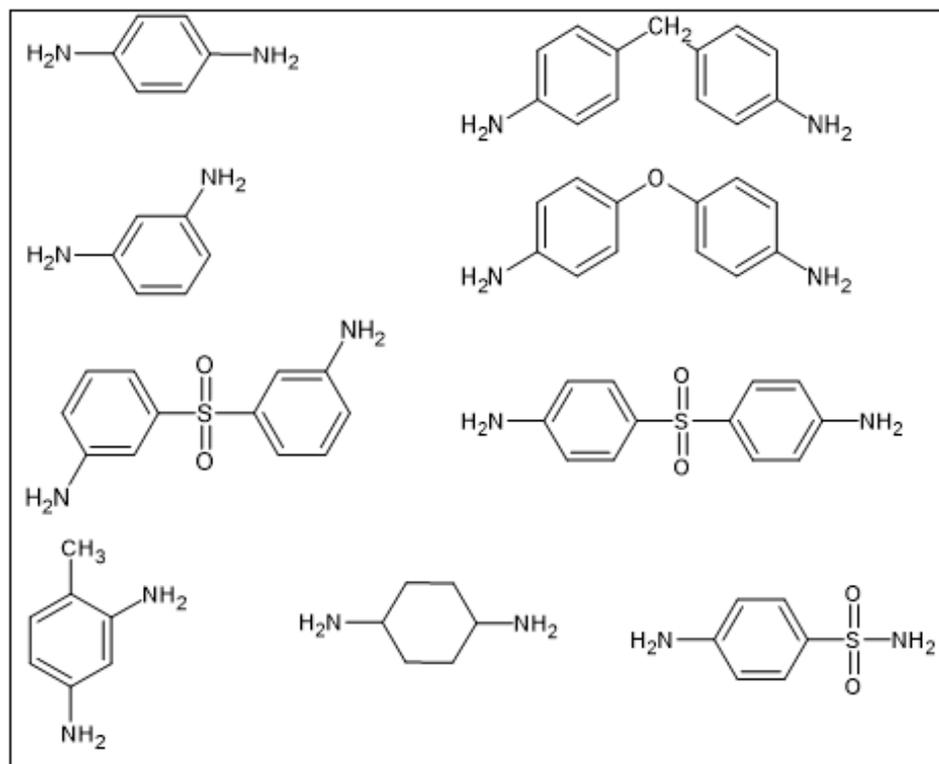
**Figure 3.** Schematic explanation of the liquid crystalline epoxy (LCE) cross-linking process.

Liquid crystal epoxy resins can be cured in several different ways, depending on the application needs and the expected final properties of the material. The main problem addressed in research on these compounds is maintaining the appropriate morphology of the hardened material. A key element influencing the arrangement of molecules in the cross-linked material is primarily the selection of the suitable monomer. However, whether the structure will have nematic or smectic characteristics also depends on the temperatures at which the entire process is carried out. The research conducted over the years suggests

that when LCER is cured within the temperature range maintaining its liquid crystal state, it tends to form an organized molecular structure [25,32].

For many years, despite attempts to introduce new hardening methods, the most popular option is still the use of hardeners. This function can be fulfilled by compounds capable of forming bonds with the oxirane ring of the liquid crystal resin. The use of aromatic amines as hardeners continues to be popular due to the speed of hardening, high efficiency, and adjustability of the properties of the final material. The reaction takes place between the epoxy ring of the liquid crystal and the amine groups of the hardener. Phenylenediamine (PDA) isomers are frequently encountered during the LCER curing procedure. The use of *m*-phenylenediamine (*m*-PDA) as a hardener causes changes in the process when the conversion of the epoxy group increases significantly in the early stage of hardening and then gradually decreases [33]. Studies indicate that *m*-PDA, in comparison to other compounds, leads to a superior alignment of liquid crystal mesogens [34]. The kinetics of the hardening reaction also depend on the stereochemical components of the hardener. The use of several *p*-phenylenediamine (*p*-PDA) derivatives with methyl group substituents at different positions on the aromatic ring reveals that the reaction proceeds most rapidly with reagents possessing the least steric hindrance [35].

Other amine compounds used in LCER hardening include diaminodiphenylmethane (4,4'-DDM), diaminodiphenyl sulfone isomers (3,3'-DDS and 4,4'-DDS) and 4,4'-oxydianiline (4,4'-ODA) [5,36–40]. The variety of hardeners used affects the final polymer network of the hardened mixture. The use of diaminodiphenylmethane will result in a more flexible network than when diaminodiphenyl sulfone is used [39]. These are examples of symmetric hardeners, eagerly used due to the possibility of creating equivalent bonds on both sides of the molecule. The mirror arrangement of atoms around the axis of the hardener theoretically results in the same susceptibility to cross-linking on either amino group. However, scientific publications also mention asymmetric compounds used to merge with liquid crystal epoxies, such as 2,4-diaminotoluene (2,4-DAT), sulfanilamide (SAA) and non-aromatic compounds such as *trans*-1,4-diaminocyclohexane (*t*-DAC) [8,39]. Some of the popular hardeners are shown in Figure 4. Changing the hardener may also result in a modification of the polymer network. The presence of diaminotoluene causes the network structure to become nematic, while the use of sulfanilamide results in the formation of a smectic phase [41,42]. The choice of the appropriate amine significantly affects the reaction mechanism and the temperature values of the processes taking place. Most hardening reactions using the above-mentioned amines occur according to the  $S_N2$  nucleophilic substitution mechanism or according to the autocatalytic mechanism. Moreover, the glass transition temperatures of hardened mixtures depend on the melting points of specific amines and their stereochemistry. The reaction kinetics also shift according to temperature changes. The reaction rate constant is higher when the process is carried out at lower temperatures [38].



**Figure 4.** Popular amine hardeners used in cross-linking with liquid crystal epoxy resins.

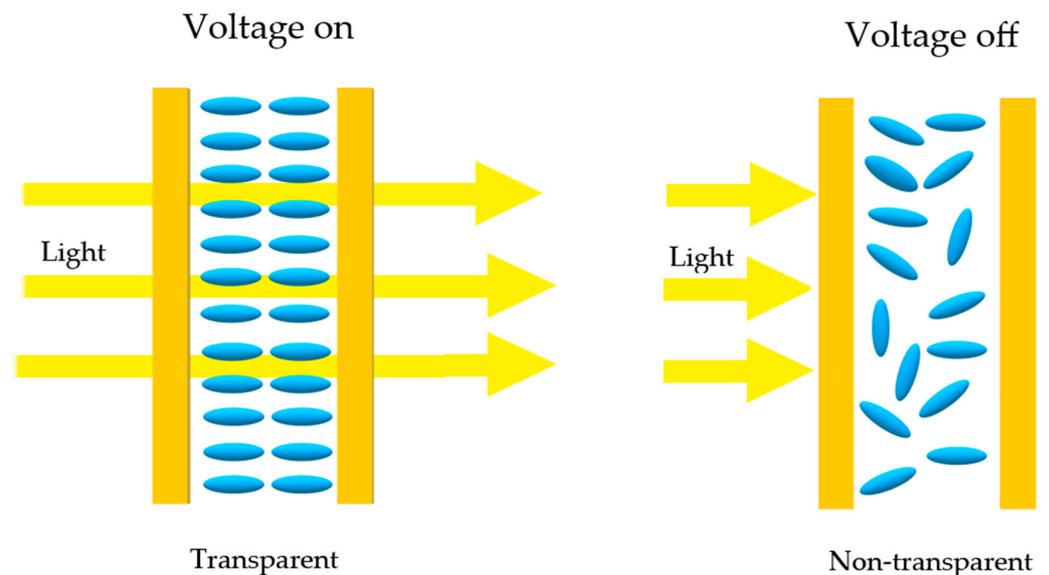
## 4. Application of Liquid Crystal Polymers

### 4.1. Non-Linear Optics

Liquid crystal epoxies find their applications in many industrial fields. One of the most frequently mentioned types of applications of these materials is using them as elements of non-linear optics. The cholesteric liquid crystals (CLCs) hold substantial significance in this context, as their helical architectural composition selectively reflects light of specific polarization, thereby inducing the phenomenon known as Bragg reflection. This ability allows for the creation of colorful patterns that shift in appearance depending on the angle of light incidence [43,44]. A similar effect can be achieved by using a liquid crystal epoxy monomer with the addition of a chiral compound. CLC mixtures are thermotropic due to the presence of a monomer, which makes them sensitive to temperature changes. Through the photopolymerization reaction of these two compounds, optical films with multicolored features are obtained. The created patterns can serve as visual entertainment, but they also hold promise for applications in counterfeit prevention [45]. Another solution to incorporate liquid crystal epoxy into mixtures with cholesteric compounds is to implant mesogenic epoxy microspheres into the CLC matrix. Research carried out in the article [46] by Zhang et al. proves that such systems are characterized by high bistability, i.e., the ability to be in one of two stable states and remain in it for a long time without the need for continuous external energy supply. This offers prospects for the production of promising materials that can be used as intelligent windows or shading elements with low energy consumption.

In the case of non-linear optics also polymer dispersive liquid crystals (PDLCs) offer an interesting application of the liquid crystallinity phenomenon. PDLC systems, better known as smart glass, are advanced materials with revolutionary properties that are used in various fields, from a wide industry range to modern screen technology. These smart materials consist of liquid crystals dispersed in a polymer in the form of droplets with a diameter often less than one micrometer [47,48]. The main attribute of these systems is their ability to control transparency in response to changes in external conditions. They are synthesized in the form of thin polymer-liquid crystal films [49] and are often used in the form of a foil

between two glass panes. An example of PDLC foil is presented in Figure 5. Under the influence of electric voltage, the arrangement of mesogens changes, giving the opportunity to control the transparency of the material [50,51]. The schematic operation of the process is presented in Figure 5. The degree of transparency of PDLC is determined by the uniformity of the droplet size and the homogeneity of their distribution in the matrix [52]. Liquid crystals dispersed in the polymer are a kind of composites of thermosetting resins and compounds with a mesogenic core [53]. Epoxy resins are often used as an element of such a composite due to their excellent electro-optical properties [54–57]. They usually function as a polymer matrix, but they can also be found in the form of a dispersed liquid crystal monomer [58]. When developing such systems, it is crucial to consider the cross-linking temperature of the composite, as it directly influences these properties [59].



**Figure 5.** PDLC foil sandwiched between two conductive plates or electrodes.

Despite their popularity, the production of stimuli-responsive liquid crystal films is a complex process that requires the use of additional conductive layers that allow for control of the display panels. Chen et al. in their study [60] present a technique for fabricating these materials that eliminates the necessity for extra layers. They manufactured LCERs within a thin film via photopolymerization, placing them directly between two electrodes. The optical properties change due to the dynamic scattering phenomenon, which happens solely in the UV-exposed area.

#### 4.2. Thermal Conductivity

Epoxy liquid crystal materials are being synthesized and examined for electronic device applications nowadays, particularly in cases where maintaining very low electrical permeability and achieving high internal thermal conductivity are crucial for ensuring optimal electromagnetic signal transmission and efficient heat dissipation [37]. In particular, the last parameter appears repeatedly in studies dealing with LCER properties. In a significant number of articles, the obtained value of the thermal conductivity coefficient ( $\lambda$ ) for liquid crystal monomers ranges from 0.29 to 0.39 W/m<sup>2</sup>K [61–63]. However, there are cases in which this coefficient reaches 0.51 W/m<sup>2</sup>K [63] or even 0.96 W/m<sup>2</sup>K [64]. The main variable determining these differences seems to be the structure of the mesogen of the liquid crystal epoxy monomer. With a focus on the improvement in this parameter, an interesting option like using diacetylene bonds in the mesogenic core was presented in the article by Hossain et al. [65]. This solution allowed the authors of this publication to increase the thermal conductivity of the material by more than twice as compared to traditional epoxy compounds. Resins containing fluorine atoms in their molecule also have appropriate parameters that ensure the possibility of use in electronics. According to research carried

out by Fan et al. [66], that kind of resin could be potentially used in electrical circuits prone to excessive heating. LCER can also be used to create fluid functional films that are characterized by both high internal thermal conductivity and excellent self-healing properties [67]. The value of the  $\lambda$  coefficient is also influenced by the length and number of carbons in the aliphatic chain of the molecule. Lv et al. in the study presented in the publication [68], noticed that liquid crystal epoxy resins with an even number of carbons in the chain that connects two mesogenic groups are distinguished by the higher thermal conductivity, and a more dense crystal structure, compared to analogous systems with an odd number of carbons.

#### 4.3. Shape Memory Polymers

In recent years, there has been an increase in scientific interest and significant progress in research on shape memory polymers (SMP), commonly known as smart materials. They demonstrate the ability to return to their original shape or properties after deformation. It can be induced by diverse external triggers, including changes in heat and electricity, availability of light, and percentage of humidity [69,70]. In particular, thermal stimuli are the most important factors according to their ability to induce internal phase changes in the polymer structure [71]. When the polymer is subjected to conditions below the glass transition temperature, it can be easily deformed, and upon the temperature rising above  $T_g$ , it returns to its original shape. This process can be cyclical, which makes such a compound attractive due to its potential for numerous application possibilities. Liquid crystal polymers (LCPs) can also exhibit shape memory properties. An example of such materials comprises blends of epoxy acrylate, which can be synthesized through the process of 3D printing [72]. LCD printing is a technique that uses the liquid crystal structure of an LCD screen to create three-dimensional objects. The fundamental characteristic of LCD printing lies in the direct passage of light through flat liquid crystal panels onto the uncured resin. Epoxy resins or their blends with other monomers can be used as the material on which printing takes place [73]. This is an example of combining the use of the liquid crystallinity phenomenon with the properties of classic epoxy resins. In this process, the material is controlled and hardened in layers to form the desired shapes. This technique facilitates the production of objects with high resolution and precise details. In addition to the obvious properties typical of SMP, such as a high shape recovery coefficient, the soft material obtained in this way is characterized by high transparency and tensile strength [74].

### 5. Liquid Crystal Epoxy Composites

Liquid crystal epoxy resins are recognized for their unique traits. However, using cross-linked LCERs alone presents challenges for broader applications. Liquid crystal composites step in to address the issue, enhancing functionality and expanding the possibilities for material aesthetics and performance. This makes exploring liquid crystal epoxy composites an increasingly intriguing area of research [63].

#### 5.1. Inorganic Fillers

Numerous studies dealing with the chemistry of liquid crystal polymers strive to balance the properties of the LC composite with its availability, and thus the costs of production on an industrial scale. Hence, inorganic compounds consistently attract interest as fillers for liquid crystal composites.

One of the nanofillers frequently employed in liquid crystal epoxy composites is boron nitride (BN) [63]. As the quantity of this compound within the LC matrix rises, the composite's glass transition temperature escalates, accompanied by a notable increase in the thermal conductivity coefficient ( $\lambda$ ). This is the result of controlled phonon scattering in the epoxy resin [75–79]. Its molecular orientation enables efficient heat transfer through phonon vibrations. Yang et al. in the study [63] proved that incorporating 30 wt% of boron nitride into liquid crystal epoxy resin doubles the coefficient value, elevating it from

0.51 W/m<sup>2</sup>K to 1.02 W/m<sup>2</sup>K. Moreover, composites containing BN are characterized by low moisture absorption and better thermomechanical properties [77]. Thanks to its nanometric scale and high specific surface area, aluminum oxide (Al<sub>2</sub>O<sub>3</sub>) is used in epoxy composite technology. Its addition can significantly improve the mechanical and thermal properties of the material [80,81]. The Al<sub>2</sub>O<sub>3</sub> content of 80 wt% of the resin increases the thermal conductivity of the composite to 1.86 W/m<sup>2</sup>K, and also slightly enhances the thermal stability of the hardened liquid crystal [81]. According to the article by Tian et al. [82] the composite containing Al<sub>2</sub>O<sub>3</sub> is characterized by a significantly reduced viscosity compared to the pure polymer and also affects the morphology of the entire mixture, increasing the order of the liquid crystal networks on a micro-scale. There are also studies combining BN and Al<sub>2</sub>O<sub>3</sub> particles to create a hybrid nanofiller. Such mixed composites are characterized by better-shaped heat transfer paths [75,83].

Another noteworthy nanofiller is barium titanate (BaTiO<sub>3</sub>). Its usefulness is related to the compound's ferromagnetic properties. BaTiO<sub>3</sub> particles are often used in PDLC composites based on epoxy resin, improving their electro-optical properties, and influencing changes in the switching voltage and the response time of the system [84–86]. Additionally, barium titanate particles influence the morphology of the entire composite, uniforming the size of liquid crystal droplets and increasing their number in the matrix. The rising concentration of this nanofiller also impacts the electronic properties of the composite. It leads, in part, to reductions in threshold voltage, saturation voltage, and the rise time of the input signal [87].

Liquid crystallinity may also be a feature attributed to the filler. This role in many nanocomposites is in some way played by graphene, mainly in the form of sheets or nanotubes [88]. Since this material is characterized by a high aspect ratio and a low percolation threshold, which means that the dispersion of just a small amount of its molecules in the polymer matrix allows the creation of long-range order in the entire composite, it is possible to use this compound in materials that have to be characterized by high conductivity or dielectric properties [89–92]. In particular, the last parameter, which could be also related to the properties of the resin [93], exists due to graphene's ability to create the LC phase. However, that kind of behavior of this compound requires the use of stabilizers to prevent the formation of agglomerates. To solve this problem, while maintaining excellent dielectric and mechanical properties, a derivative of this popular filler, graphene oxide (GO) can be used [94–96]. The nematic liquid crystal phase in GO forms spontaneously and remains in the same phase after mixing with the polymer matrix [97,98]. To maintain such a structure, a directed magnetic field is used giving the material the desired orientation. The appropriate morphology of the composite can be additionally ensured by the use of graphene oxide combined with iron oxide nanoparticles (GO-IONP) [99,100]. GO also appears in the context of improving the tribological properties of composites. It has been shown that a relatively small content of graphene oxide significantly increases the mentioned properties [101,102].

The need to produce multifunctional integrated composites in modern liquid crystal chemistry leads to the synthesis of nanofillers directly in the epoxy matrix. Ag-coated diamond nanoparticles hold potential in this aspect [103]. The diamond itself is characterized by several excellent properties such as thermal conductivity, electrical insulation, and a low coefficient of thermal expansion—CTE [104,105]. The presence of diamond/Ag particles initiates the formation of connections in the composite network at the quantum level, creating heat conduction paths and thus demonstrating a significant  $\lambda$  value (4.65 W/m<sup>2</sup>K) and thermal stability. An innovative idea was presented by Zhang et al. in the publication [106] by synthesizing hybrid fillers combining nanodiamond particles with graphite nanoplatelets (ND@GNP). In these studies, a reduction in the molecular movement of the entire epoxy composite was noticed, which significantly improved its thermophysical properties, creating prospects for wider application.

## 5.2. Other Composites

In liquid crystal epoxy composites, functionalized mesoporous silica (SBA) can also be used as a nanofiller. Its presence in the matrix ensures a lower dielectric constant and better hydrophobicity of the material [107]. Another proposition in the synthesis of composites is the use of amino carbon nanotubes with hexagonal boron nitride (h-BN@MCNT-NH<sub>2</sub>). The advantage of this complex hybrid filler is that the amino group contained in its structure takes part in the hardening of the liquid crystal epoxy resin. Additionally, its mixed composition reduces the interfacial thermal resistance, which improves the thermal conductivity of the final material [108].

In the recent scientific literature, there are cases of blends comprising liquid crystal epoxy resins and conventional epoxy resins. Combining two components with the same functional groups not only improves the performance of the resin itself but also avoids the negative effects caused sometimes by inorganic fillers [109]. Due to the presence of the rigid segments of mesogenic units in the liquid crystal and their substantial degree of organization, the available space within the hardened composite network diminishes, leading to a heightened cross-linking density in the resultant product. Consequently, this density growth substantially enhances the thermal stability of the system along with its thermal conductivity [109]. The liquid crystal phase can be stabilized with epoxy resin particles. Chen et al., in their work [110] synthesized this type of composite, which is characterized by high tolerance to stress and is used in the technology of energy-efficient smart windows.

An appealing substitute for conventional plastics comes in the form of vitrimers. They boast similar mechanical properties to thermosetting materials and additionally can alter shape and self-heal surface damage [111]. The common element connecting them with the issue of liquid crystallinity is their application in the field of optical and semiconductor materials. Both types of compounds can be used to produce advanced electronic components, including integrated circuits, and for various optical applications, such as lenses, LCD screens, and lasers. The inclusion of mesogenic domains from liquid crystal epoxy resin into the vitrimer structure enables compounds of this type to be cross-linked at higher temperatures while retaining properties typical of elastomers. This also enables easier processing of the final material and the possibility of reprocessing it [39,112]. The research presented in the article [113] showed that the vitrimerization reaction taking place with the participation of a liquid crystal epoxy resin having ester and imine groups in its structure leads to the production of a compound that can be chemically recycled. This is possible thanks to the metathesis reactions and transesterification of each imine and ester group, which are the basis of the vitrimerization process. The material recycled after processing maintains its mechanical and thermal properties.

## 6. Conclusions

In conclusion, this work presents an overview of research focusing on liquid crystal materials published in recent years. Scientific development in the field of LCER is largely based on modifications involving hardeners, especially aromatic amines. The influence of the mesogen structure of liquid crystal compounds on the entire epoxy network was also discussed. The wide range of fillers presented in this article is evidence of researchers' focus on the practical use of LC compounds in industry. The unique properties assigned to them offer improved mechanical, thermal, and optical properties, paving the way for next-generation materials. Liquid crystals are promising compounds in the field of materials science, and represent the future of technological development. While waiting for their dynamic development from year to year, we are witnessing a constant search for new applications and improvements that can bring a significant contribution to the field of science and industry. With the growing scientific and technological interest, research on liquid crystal materials continues to lead to the discovery of new possibilities for their use and improvement in their properties, which can bring significant progress in various areas of life.

**Author Contributions:** Conceptualization, W.Z.; resources, W.Z.; writing—original draft preparation, W.Z.; writing—review and editing, W.Z., M.K. and B.M.-L.; funding acquisition, B.M.-L. and M.K. All authors have read and agreed to the published version of the manuscript.

**Funding:** Financed by the Minister of Science and Higher Education Republic of Poland within the program “Regional Excellence Initiative”.

**Data Availability Statement:** No new data were created or analyzed in this review. Data sharing is not applicable to this article.

**Conflicts of Interest:** The authors declare no conflicts of interest.

## References

1. Zheng, R.; Ma, L.; Feng, W.; Pan, J.; Wang, Z.; Chen, Z.; Zhang, Y.; Li, C.; Chen, P.; Bisoyi, H.K.; et al. Autonomous Self-Sustained Liquid Crystal Actuators Enabling Active Photonic Applications. *Adv. Funct. Mater.* **2023**, *33*, 2301142. [\[CrossRef\]](#)
2. Sun, J.; Wang, C.; Liu, Y.; Liang, X.; Wang, Z. Liquid Crystal Elastomer Composites for Soft Actuators. *Int. J. Smart Nano Mater.* **2023**, *14*, 440–459. [\[CrossRef\]](#)
3. Maurin, V.; Chang, Y.; Ze, Q.; Leanza, S.; Wang, J.; Zhao, R.R. Liquid Crystal Elastomer–Liquid Metal Composite: Ultrafast, Untethered, and Programmable Actuation by Induction Heating. *Adv. Mater.* **2023**, 2302765. [\[CrossRef\]](#) [\[PubMed\]](#)
4. Chauhan, G.; Malik, P.; Deep, A. Morphological, Dielectric, Electro-Optic and Photoluminescence Properties of Titanium Oxide Nanoparticles Enriched Polymer Stabilized Cholesteric Liquid Crystal Composites. *J. Mol. Liq.* **2023**, *376*, 121406. [\[CrossRef\]](#)
5. Harada, M.; Ando, J.; Yamaki, M.; Ochi, M. Synthesis, Characterization, and Mechanical Properties of a Novel Terphenyl Liquid Crystalline Epoxy Resin. *J. Appl. Polym. Sci.* **2015**, *132*, 41296. [\[CrossRef\]](#)
6. Zhong, X.; Yang, X.; Ruan, K.; Zhang, J.; Zhang, H.; Gu, J. Discotic Liquid Crystal Epoxy Resins Integrating Intrinsic High Thermal Conductivity and Intrinsic Flame Retardancy. *Macromol. Rapid Commun.* **2022**, *43*, 2100580. [\[CrossRef\]](#) [\[PubMed\]](#)
7. Olamilekan, A.I.; Yeo, H. Thermal Conducting Thermosets Driven by Molecular Structurally Enhanced Mesogen Interactions. *ACS Appl. Polym. Mater.* **2021**, *3*, 4147–4155. [\[CrossRef\]](#)
8. Li, Y.; Ambroggi, V.; Cerruti, P.; Goswami, M.; Yang, Z.; Kessler, M.R.; Rios, O. Functional Liquid Crystalline Epoxy Networks and Composites: From Materials Design to Applications. *Int. Mater. Rev.* **2022**, *67*, 201–229. [\[CrossRef\]](#)
9. Harada, M.; Hirotsu, M.; Ochi, M. Synthesis and Improved Mechanical Properties of Twin-Mesogenic Epoxy Thermosets Using Siloxane Spacers with Different Lengths. *J. Appl. Polym. Sci.* **2019**, *136*, 47891. [\[CrossRef\]](#)
10. Lee, M.; Ha, M.Y.; Lee, M.; Kim, J.H.; Kim, S.D.; Kim, I.; Lee, W.B. Aligned Structures of Mesogenic Motifs in Epoxy Resin and Their Thermal Conductivities. *Nanoscale Adv.* **2022**, *4*, 1970–1978. [\[CrossRef\]](#)
11. Uchida, J.; Soberats, B.; Gupta, M.; Kato, T. Advanced Functional Liquid Crystals. *Adv. Mater.* **2022**, *34*, 2109063. [\[CrossRef\]](#)
12. Li, Y.; Liu, T.; Ambroggi, V.; Rios, O.; Xia, M.; He, W.; Yang, Z. Liquid Crystalline Elastomers Based on Click Chemistry. *ACS Appl. Mater. Interfaces* **2022**, *14*, 14842–14858. [\[CrossRef\]](#) [\[PubMed\]](#)
13. Fang, H.; Zhang, F.; Zhao, Y.; Gao, X.; Zhou, W.; Qi, G.; Ding, Y.; Winter, H.H. Rheology of Smectic Liquid Crystalline Elastomers with Dynamic Covalent Bonds. *Macromolecules* **2023**, *56*, 7808–7817. [\[CrossRef\]](#)
14. Wang, Z.; Cai, S. Recent Progress in Dynamic Covalent Chemistries for Liquid Crystal Elastomers. *J. Mater. Chem. B* **2020**, *8*, 6610–6623. [\[CrossRef\]](#) [\[PubMed\]](#)
15. Zhu, Y.; Xu, Z.; Wu, F.; Wang, M.; Chen, L. Liquid-Crystal Elastomers Based on Covalent Adaptable Networks: From Molecular Design to Applications. *Sci. China Mater.* **2023**, *66*, 3004–3021. [\[CrossRef\]](#)
16. Utekar, S.; Suriya, V.K.; More, N.; Rao, A. Comprehensive Study of Recycling of Thermosetting Polymer Composites—Driving Force, Challenges and Methods. *Compos. B Eng.* **2021**, *207*, 108596. [\[CrossRef\]](#)
17. Mahmoudi, M.; Burlison, S.R.; Moreno, S.; Minary-Jolandan, M. Additive-Free and Support-Free 3D Printing of Thermosetting Polymers with Isotropic Mechanical Properties. *ACS Appl. Mater. Interfaces* **2021**, *13*, 5529–5538. [\[CrossRef\]](#) [\[PubMed\]](#)
18. Shundo, A.; Aoki, M.; Yamamoto, S.; Tanaka, K. Cross-Linking Effect on Segmental Dynamics of Well-Defined Epoxy Resins. *Macromolecules* **2021**, *54*, 5950–5956. [\[CrossRef\]](#)
19. Di-wu, J.; Zhou, W.; Wang, Y.; Li, Y.; Lv, Y.; Zhang, Y.; Zhang, N.; Chen, Q. Synergetic Improvements of Intrinsic Thermal Conductivity and Breakdown Strength in Liquid Crystal Epoxy Resin for High Voltage Applications. *J. Polym. Res.* **2024**, *31*, 72. [\[CrossRef\]](#)
20. Shiota, A.; Ober, C.K. Synthesis and Curing of Novel LC Twin Epoxy Monomers for Liquid Crystal Thermosets. *J. Polym. Sci. A Polym. Chem.* **1996**, *34*, 1291–1303. [\[CrossRef\]](#)
21. Barclay, G.G.; Ober, C.K.; Papathomas, K.I.; Wang, D.W. Liquid Crystalline Epoxy Thermosets Based on Dihydroxymethylstilbene: Synthesis and Characterization. *J. Polym. Sci. A Polym. Chem.* **1992**, *30*, 1831–1843. [\[CrossRef\]](#)
22. Zhou, W.; Wang, Y.; Kong, F.; Peng, W.; Wang, Y.; Yuan, M.; Han, X.; Liu, X.; Li, B. Advances in Liquid Crystal Ep Molecular Structures, Thermal Conductivity, and Promising Applications in Thermal Management. *Energy Environ. Mater.* **2024**, e12698. [\[CrossRef\]](#)
23. Ruan, K.; Zhong, X.; Shi, X.; Dang, J.; Gu, J. Liquid Crystal Epoxy Resins with High Intrinsic Thermal Conductivities and Their Composites: A Mini-Review. *Mater. Today Phys.* **2021**, *20*, 100456. [\[CrossRef\]](#)

24. Kawamoto, S.; Fujiwara, H.; Nishimura, S. Hydrogen Characteristics and Ordered Structure of Mono-Mesogen Type Liquid-Crystalline Epoxy Polymer. *Int. J. Hydrogen Energy* **2016**, *41*, 7500–7510. [[CrossRef](#)]
25. Hong, Y.; Goh, M. Advances in Liquid Crystalline Epoxy Resins for High Thermal Conductivity. *Polymers* **2021**, *13*, 1302. [[CrossRef](#)] [[PubMed](#)]
26. Kisiel, M.; Mossety-Leszczak, B. The Effect of Nonterminal Liquid Crystalline Epoxy Resin Structure and Curing Agents on the Glass Transition of Polymer Networks. *Polymers* **2024**, *16*, 857. [[CrossRef](#)] [[PubMed](#)]
27. Harada, M.; Okamoto, N.; Ochi, M. Influence of the Introduction of Flexible Alkyl Chains on the Thermal Behavior and Mechanical Properties of Mesogenic Epoxy Thermosets. *J. Appl. Polym. Sci.* **2016**, *133*, 44244. [[CrossRef](#)]
28. Lin, Z.; Cong, Y.; Zhang, B.; Huang, H. Synthesis and Characterisation of a Novel Y-Shaped Liquid Crystalline Epoxy and Its Effect on Isotropic Epoxy Resin. *Liq. Cryst.* **2019**, *46*, 1467–1477. [[CrossRef](#)]
29. Zhu, S.; Li, W.; Lu, B.; Chen, W.; Zhang, W.; Niu, X.; Chen, X.; An, Z. Evaluation of Mesomorphic and Thermal Stabilities for Terminal Epoxy Liquid Crystals. *J. Mol. Liq.* **2020**, *317*, 113955. [[CrossRef](#)]
30. Harada, M.; Yokoyama, Y.; Ochi, M. Synthesis of Multifunctional Liquid Crystalline Epoxy Resin Embedded Cyclic-Siloxane Chain with  $T_g$ -Less Behavior and Enhanced Toughness. *High Perform. Polym.* **2021**, *33*, 3–11. [[CrossRef](#)]
31. Trinh, T.E.; Yeo, H. Enhancement of Thermal Conducting Properties in Epoxy Thermoset Systems Using an Aligned Liquid-Crystalline Mesophase. *Mater. Adv.* **2024**, *5*, 1702–1714. [[CrossRef](#)]
32. Carfagna, C.; Amendola, E.; Giamberini, M. Liquid Crystalline Epoxy Based Polymers. *Prog. Polym. Sci.* **1997**, *22*, 1607–1647. [[CrossRef](#)]
33. Harada, M.; Yamaguchi, K. Fracture Toughness of Highly Ordered Liquid Crystalline Epoxy Thermosets Achieved by Optimized Composition of Curing Agents. *J. Appl. Polym. Sci.* **2021**, *138*, 53–56. [[CrossRef](#)]
34. Harada, M.; Matsumoto, T. Thermal Conductivity and Orientation Structure of Liquid Crystalline Epoxy Thermosets Prepared by Latent Curing Catalyst. *Crystals* **2024**, *14*, 47. [[CrossRef](#)]
35. Olamilekan, A.I.; Yeo, H. Curing Behavior of 4,4'-Diglycidylloxybiphenyl with p-Phenylene Diamine Derivatives. *Macromol. Res.* **2020**, *28*, 960–967. [[CrossRef](#)]
36. Wu, W.; Li, Z.; Zhang, B. Rational Design and Synthesis of a Novel LCE Material and Its Curing Behaviours. *Liq. Cryst.* **2021**, *48*, 1723–1732. [[CrossRef](#)]
37. Zhang, J.; Dang, L.; Zhang, F.; Zhang, K.; Kong, Q.; Gu, J. Effect of the Structure of Epoxy Monomers and Curing Agents: Toward Making Intrinsically Highly Thermally Conductive and Low-Dielectric Epoxy Resins. *JACS Au* **2023**, *3*, 3424–3435. [[CrossRef](#)] [[PubMed](#)]
38. Yeo, H. Curing Kinetics of Liquid Crystalline 4,4'-Diglycidylloxybiphenyl Epoxy with Various Diamines. *Polymer* **2019**, *168*, 209–217. [[CrossRef](#)]
39. Hoekstra, D.C.; Schenning, A.P.H.J.; Debijs, M.G. Epoxide and Oxetane Based Liquid Crystals for Advanced Functional Materials. *Soft Matter* **2020**, *16*, 5106–5119. [[CrossRef](#)] [[PubMed](#)]
40. Jilani, W.; Fourati, N.; Zerrouki, C.; Faugeras, P.A.; Guinault, A.; Zerrouki, R.; Guermazi, H. Exploring the Structural Properties and Enhancement of Opto-Electrical Investigations for the Synthesized Epoxy Based Polymers with Local Nanoscale Structures. *Mater. Res. Express* **2020**, *7*, 35305. [[CrossRef](#)]
41. Amendola, E.; Carfagna, C.; Giamberini, M.; Pisaniello, G. Curing Reactions of a Liquid Crystalline Epoxy Resin Based on the Diglycidyl Ether of 4,4'-dihydroxy- $\alpha$ -methylstilbene. *Macromol. Chem. Phys.* **1995**, *196*, 1577–1591. [[CrossRef](#)]
42. Lin, Q.; Yee, A.F.; Earls, J.D.; Hefner, R.E.; Sue, H.J. Phase Transformations of a Liquid Crystalline Epoxy during Curing. *Polymer* **1994**, *35*, 2679–2682. [[CrossRef](#)]
43. Zhang, Z.; Chen, Z.; Wang, Y.; Zhao, Y.; Shang, L. Cholesteric Cellulose Liquid Crystals with Multifunctional Structural Colors. *Adv. Funct. Mater.* **2022**, *32*, 2107242. [[CrossRef](#)]
44. Wani, O.M.; Schenning, A.P.H.J.; Priimagi, A. A Bifacial Colour-Tunable System: Via Combination of a Cholesteric Liquid Crystal Network and Hydrogel. *J. Mater. Chem. C Mater.* **2020**, *8*, 10191–10196. [[CrossRef](#)]
45. Zhang, X.; Guo, Y.; Li, Y.; Liu, W.; Li, H.; Yang, Y. Colorfully Patterned Epoxy Resin Films with a Cholesteric Structure Prepared through a Photopolymerization Approach. *ACS Appl. Polym. Mater.* **2022**, *5*, 193–200. [[CrossRef](#)]
46. Zhang, H.; Li, F.; Zhang, R.; Deng, Z.; Ma, Y.; He, Z.; Fang, F.; Miao, Z.; Shen, W. Fabrication of Mesogenic Epoxy Microsphere-Filled Negative-Dielectric-Anisotropy Cholesteric Liquid Crystals for Bistable Devices. *J. Mol. Liq.* **2023**, *384*, 122255. [[CrossRef](#)]
47. Higgins, D.A. Probing the Mesoscopic Chemical and Physical Properties of Polymer-Dispersed Liquid Crystals. *Adv. Mater.* **2000**, *12*, 251–264. [[CrossRef](#)]
48. Zhao, Y.; He, Z.; Ban, Q.; Li, K.; Ding, S.; Tian, S.; Ren, H.; Zhu, M.; Ma, Q.; Miao, Z. Study on the Electro-Optical Properties of Epoxy Resin Based Polymer Dispersed Liquid Crystal Films. *Mol. Cryst. Liq. Cryst.* **2021**, *722*, 1–7. [[CrossRef](#)]
49. Li, Y.; Gong, C.; Li, C.; Ruan, K.; Liu, C.; Liu, H.; Gu, J. Liquid Crystalline Texture and Hydrogen Bond on the Thermal Conductivities of Intrinsic Thermal Conductive Polymer Films. *J. Mater. Sci. Technol.* **2021**, *82*, 250–256. [[CrossRef](#)]
50. Wu, K.; Sun, J.J.; Meng, F.; Fan, M.; Kong, X.; Cai, M.; Zhao, T.; Yang, C.; Xin, Y.; Xing, J.; et al. Highly Flexible and Electrically Controlled Grating Enabled by Polymer Dispersed Liquid Crystal. *J. Mol. Liq.* **2022**, *353*, 118664. [[CrossRef](#)]
51. Lin, H.; Zhao, Y.; Jiao, X.; Gao, H.; Guo, Z.; Wang, D.; Luan, Y.; Wang, L. Preparation and Application of Polymer-Dispersed Liquid Crystal Film with Step-Driven Display Capability. *Molecules* **2024**, *29*, 1109. [[CrossRef](#)]

52. AcademicJayoti, D.; Malik, P.; Singh, A. Analysis of Morphological Behaviour and Electro-Optical Properties of Silica Nanoparticles Doped Polymer Dispersed Liquid Crystal Composites. *J. Mol. Liq.* **2017**, *225*, 456–461. [[CrossRef](#)]
53. Sun, Y.; Zhang, C.; Zhou, L.; Fang, H.; Huang, J.; Ma, H.; Zhang, Y.; Yang, J.; Zhang, L.Y.; Song, P.; et al. Effect of a Polymercaptan Material on the Electro-Optical Properties of Polymer-Dispersed Liquid Crystal Films. *Molecules* **2017**, *22*, 43. [[CrossRef](#)] [[PubMed](#)]
54. Ellahi, M.; Taimur, S.; Baloch, N.; Bhayo, A.M.; Sarwar, A.; Qadar, F. Study of Polymer-Dispersed Liquid Crystal (PDLC) Thin Film Technology for Smart Electronic Devices. *J. Electron. Mater.* **2024**, *53*, 1094–1104. [[CrossRef](#)]
55. Jilani, W.; Bouzidi, A.; Elleuch, S.; Guermazi, H. Synthesis, Morphology, Vibrational, and Physical Characterization of DGEBA Epoxy Doped Liquid Crystal Organic Polymeric Systems (EDLCPs) for High-Performance Embedded Capacitors. *Opt. Quantum Electron.* **2024**, *56*, 617. [[CrossRef](#)]
56. Lin, H.; Zhang, S.; Saeed, M.H.; Zhou, L.; Gao, H.; Huang, J.; Zhang, L.; Yang, H.; Xiao, J.; Gao, Y. Effects of the Methacrylate Monomers with Different End Groups on the Morphologies, Electro-Optical and Mechanical Properties of Polymer Dispersed Liquid Crystals Composite Films. *Liq. Cryst.* **2021**, *48*, 722–734. [[CrossRef](#)]
57. Jilani, W.; Bouzidi, A.; Hamdi, R.; Al-Dossari, M.; Yahia, I.S.; Guermazi, H. Experimental Investigations of DGEBA Epoxy Resin Dispersed Liquid Crystal Polymer Systems for the Development of New Electronic Devices. *J. Mol. Liq.* **2024**, *395*, 123923. [[CrossRef](#)]
58. Saeed, M.H.; Zhang, S.; Cao, Y.; Zhou, L.; Hu, J.; Muhammad, I.; Xiao, J.; Zhang, L.; Yang, H. Recent Advances in the Polymer Dispersed Liquid Crystal Composite and Its Applications. *Molecules* **2020**, *25*, 5510. [[CrossRef](#)] [[PubMed](#)]
59. Chen, G.; Hu, W.; Zhou, L.; Zhang, H.; Wang, L.; Zhang, C.; Sun, J.; Zhang, L.; Yuan, X.; Zhu, S. The Electro-Optical Properties and Adhesion Strength of Epoxy- Polymercaptan-Based Polymer Dispersed Liquid Crystal Films. *Crystals* **2021**, *11*, 576. [[CrossRef](#)]
60. Chen, G.; Zhang, J.; Ren, Y.; Sun, C.; Hu, W.; Yang, H.; Yang, D.K. Programmable Patterned Dynamic Scattering of Liquid Crystals/Epoxy-Based Polymer Composite Film Sandwiched between Two Fully Covered Electrodes. *Adv. Opt. Mater.* **2023**, *11*, 2300537. [[CrossRef](#)]
61. Harada, M.; Hamaura, N.; Ochi, M.; Agari, Y. Thermal Conductivity of Liquid Crystalline Epoxy/BN Filler Composites Having Ordered Network Structure. *Compos. B Eng.* **2013**, *55*, 306–313. [[CrossRef](#)]
62. Guo, H.; Lu, M.; Liang, L.; Wu, K.; Ma, D.; Xue, W. Liquid Crystalline Epoxies with Lateral Substituents Showing a Low Dielectric Constant and High Thermal Conductivity. *J. Electron. Mater.* **2017**, *46*, 982–991. [[CrossRef](#)]
63. Yang, X.; Zhu, J.; Yang, D.; Zhang, J.; Guo, Y.; Zhong, X.; Kong, J.; Gu, J. High-Efficiency Improvement of Thermal Conductivities for Epoxy Composites from Synthesized Liquid Crystal Epoxy Followed by Doping BN Fillers. *Compos. B Eng.* **2020**, *185*, 107784. [[CrossRef](#)]
64. Akatsuka, M.; Takezawa, Y. Study of High Thermal Conductive Epoxy Resins Containing Controlled High-Order Structures. *J. Appl. Polym. Sci.* **2003**, *89*, 2464–2467. [[CrossRef](#)]
65. Hossain, M.M.; Olamilekan, A.I.; Jeong, H.O.; Lim, H.; Kim, Y.K.; Cho, H.; Jeong, H.D.; Islam, M.A.; Goh, M.; You, N.H.; et al. Diacetylene-Containing Dual-Functional Liquid Crystal Epoxy Resin: Strategic Phase Control for Topochemical Polymerization of Diacetylenes and Thermal Conductivity Enhancement. *Macromolecules* **2022**, *55*, 4402–4410. [[CrossRef](#)]
66. Fan, X.; Liu, Z.; Wang, S.; Gu, J. Low Dielectric Constant and Highly Intrinsic Thermal Conductivity Fluorine-containing Epoxy Resins with Ordered Liquid Crystal Structures. *SusMat* **2023**, *3*, 877–893. [[CrossRef](#)]
67. Yang, X.; Zhong, X.; Zhang, J.; Gu, J. Intrinsic High Thermal Conductive Liquid Crystal Epoxy Film Simultaneously Combining with Excellent Intrinsic Self-Healing Performance. *J. Mater. Sci. Technol.* **2021**, *68*, 209–215. [[CrossRef](#)]
68. Lv, G.; Shen, C.; Shan, N.; Jensen, E.; Li, X.; Evans, C.M.; Cahill, D.G. Odd–Even Effect on the Thermal Conductivity of Liquid Crystalline Epoxy Resins. *Proc. Natl. Acad. Sci. USA* **2022**, *119*, e2211151119. [[CrossRef](#)] [[PubMed](#)]
69. Wang, J.; Xue, Z.; Li, G.; Wang, Y.; Fu, X.; Zhong, W. UV-Curable Epoxy with “Soft” Segments for 3D-Printable Shape-Memory Materials. *J. Mater. Sci.* **2018**, *53*, 12650–12661. [[CrossRef](#)]
70. Ge, Q.; Sakhaei, A.H.; Lee, H.; Dunn, C.K.; Fang, N.X. Multimaterial 4D Printing with Tailorable Shape Memory Polymers. *Sci. Rep.* **2016**, *6*, 31110. [[CrossRef](#)]
71. Lee, A.Y.; An, J.; Chua, C.K. Two-Way 4D Printing: A Review on the Reversibility of 3D-Printed Shape Memory Materials. *Engineering* **2017**, *3*, 663–674. [[CrossRef](#)]
72. Tosto, C.; Saitta, L.; Latteri, A.; Cicala, G. Epoxy-Based Blend Formulation for Dual Curing in Liquid Crystal Display 3D Printing: A Study on Thermomechanical Properties Variation for Enhanced Printability. *Polymers* **2024**, *16*, 358. [[CrossRef](#)] [[PubMed](#)]
73. Tosto, C.; Pergolizzi, E.; Blanco, I.; Patti, A.; Holt, P.; Karmel, S.; Cicala, G. Epoxy Based Blends for Additive Manufacturing by Liquid Crystal Display (LCD) Printing: The Effect of Blending and Dual Curing on Daylight Curable Resins. *Polymers* **2020**, *12*, 1594. [[CrossRef](#)] [[PubMed](#)]
74. Shan, W.; Chen, Y.; Hu, M.; Qin, S.; Liu, P. 4D Printing of Shape Memory Polymer via Liquid Crystal Display (LCD) Stereolithographic 3D Printing. *Mater. Res. Express* **2020**, *7*, 105305. [[CrossRef](#)]
75. AbdulKarim-Talaq, M.; Hassan, K.T.; Hameed, D.A. Improvement of Thermal Conductivity of Novel Asymmetric Dimeric Coumarin Liquid Crystal by Doping with Boron Nitride and Aluminium Oxide Nanoparticles. *Mater. Chem. Phys.* **2023**, *297*, 127367. [[CrossRef](#)]
76. Zhu, Z.; Li, C.; Songfeng, E.; Xie, L.; Geng, R.; Lin, C.T.; Li, L.; Yao, Y. Enhanced Thermal Conductivity of Polyurethane Composites via Engineering Small/Large Sizes Interconnected Boron Nitride Nanosheets. *Compos. Sci. Technol.* **2019**, *170*, 93–100. [[CrossRef](#)]

77. Feng, Z.; Liu, J.; Chen, X. Liquid Crystal Epoxy Composites Based on Functionalized Boron Nitride: Synthesis and Thermal Properties. *Polym. Eng. Sci.* **2023**, *63*, 932–942. [[CrossRef](#)]
78. Li, Y.; Wu, Y.; Huang, X.; Gong, C.; Shi, Q.; Zhou, W.; Cheng, Q. Flexible and Thermally Conductive Epoxy-Dispersed Liquid Crystal Composites Filled with Functionalized Boron Nitride Nanosheets. *Polym. Compos.* **2023**, *44*, 6581–6592. [[CrossRef](#)]
79. Wu, L.C.; Huang, Y.W.; Yeh, Y.M.; Lin, C.H. Characteristic and Synthesis of High-Temperature Resistant Liquid Crystal Epoxy Resin Containing Boron Nitride Composite. *Polymers* **2022**, *14*, 1252. [[CrossRef](#)]
80. Chen, C.; Xue, Y.; Li, X.; Wen, Y.; Liu, J.; Xue, Z.; Shi, D.; Zhou, X.; Xie, X.; Mai, Y.W. High-Performance Epoxy/Binary Spherical Alumina Composite as Underfill Material for Electronic Packaging. *Compos. Part A Appl. Sci. Manuf.* **2019**, *118*, 67–74. [[CrossRef](#)]
81. Zhang, Q.; Chen, G.; Wu, K.; Shi, J.; Liang, L.; Lu, M. Biphenyl Liquid Crystal Epoxy Containing Flexible Chain: Synthesis and Thermal Properties. *J. Appl. Polym. Sci.* **2020**, *137*, e49143. [[CrossRef](#)]
82. Tian, F.; Cao, J.; Ma, W. Enhanced Thermal Conductivity and Rheological Performance of Epoxy and Liquid Crystal Epoxy Composites with Filled Al<sub>2</sub>O<sub>3</sub> Compound. *Polym. Test.* **2023**, *120*, 107940. [[CrossRef](#)]
83. Sanchez, W.A.L.; Huang, C.Y.; Chen, J.X.; Soong, Y.C.; Chan, Y.N.; Chiou, K.C.; Lee, T.M.; Cheng, C.C.; Chiu, C.W. Enhanced Thermal Conductivity of Epoxy Composites Filled with Al<sub>2</sub>O<sub>3</sub>/Boron Nitride Hybrids for Underfill Encapsulation Materials. *Polymers* **2021**, *13*, 147. [[CrossRef](#)]
84. Ahmad, F.; Jeon, Y.J.; Jamil, M. Characteristics of Extra Polymer Layer Doped with (BaTiO<sub>3</sub>) Nanoparticles: Polymer Dispersed Liquid Crystal Display. *Optoelectron. Adv. Mater. Rapid Commun.* **2018**, *12*, 491–494.
85. Rao Darla, M.; Hegde, S.; Varghese, S. Effect of BaTiO<sub>3</sub> Nanoparticle on Electro-Optical Properties of Polymer Dispersed Liquid Crystal Displays. *J. Cryst. Process Technol.* **2014**, *04*, 60–63. [[CrossRef](#)]
86. Shim, H.; Lyu, H.K.; Allabergenov, B.; Garbovskiy, Y.; Glushchenko, A.; Choi, B. Enhancement of Frequency Modulation Response Time for Polymer-Dispersed Liquid Crystal. *Liq. Cryst.* **2016**, *43*, 1390–1396. [[CrossRef](#)]
87. Kumari, A.; Sinha, A. Role of BaTiO<sub>3</sub> Nanoparticles on Electro-Optic Performance of Epoxy-Resin-Based PDLC Devices. *Liq. Cryst.* **2021**, *48*, 23–34. [[CrossRef](#)]
88. Burger, N.; Laachachi, A.; Ferriol, M.; Lutz, M.; Toniazzi, V.; Ruch, D. Review of Thermal Conductivity in Composites: Mechanisms, Parameters and Theory. *Prog. Polym. Sci.* **2016**, *61*, 1–28. [[CrossRef](#)]
89. Nan, C.W.; Shen, Y.; Ma, J. Physical Properties of Composites near Percolation. *Annu. Rev. Mater. Res.* **2010**, *40*, 131–151. [[CrossRef](#)]
90. Nassira, H.; Sánchez-Ferrer, A.; Adamcik, J.; Handschin, S.; Mahdavi, H.; Taheri Qazvini, N.; Mezzenga, R. Gelatin–Graphene Nanocomposites with Ultralow Electrical Percolation Threshold. *Adv. Mater.* **2016**, *28*, 6914–6920. [[CrossRef](#)]
91. Han, N.M.; Wang, Z.; Shen, X.; Wu, Y.; Liu, X.; Zheng, Q.; Kim, T.H.; Yang, J.; Kim, J.K. Graphene Size-Dependent Multifunctional Properties of Unidirectional Graphene Aerogel/Epoxy Nanocomposites. *ACS Appl. Mater. Interfaces* **2018**, *10*, 6580–6592. [[CrossRef](#)]
92. Nistal, A.; Garcia, E.; Pérez-Coll, D.; Prieto, C.; Belmonte, M.; Osendi, M.I.; Miranzo, P. Low Percolation Threshold in Highly Conducting Graphene Nanoplatelets/Glass Composite Coatings. *Carbon* **2018**, *139*, 556–563. [[CrossRef](#)]
93. Włodarska, M.; Mossety-Leszczak, B.; Bąk, G.W.; Kisiel, M.; Dłużniewski, M.; Okrasa, L. Epoxy Matrix with Triaromatic Mesogenic Unit in Dielectric Spectroscopy Observation. *Spectrochim. Acta A Mol. Biomol. Spectrosc.* **2018**, *194*, 102–110. [[CrossRef](#)] [[PubMed](#)]
94. Cheng, Z.; Wang, T.; Li, X.; Zhang, Y.; Yu, H. NIR-Vis-UV Light-Responsive Actuator Films of Polymer-Dispersed Liquid Crystal/Graphene Oxide Nanocomposites. *ACS Appl. Mater. Interfaces* **2015**, *7*, 27494–27501. [[CrossRef](#)] [[PubMed](#)]
95. Hu, B.; Cong, Y.H.; Zhang, B.Y.; Zhang, L.; Huang, H.Z. Comparison of Two Kinds of Liquid Crystalline Monomers with Different Mesogenic Units Grafted Graphene Oxide on Thermal and Mechanical Properties of Epoxy Nanocomposite Materials. *Liq. Cryst.* **2021**, *48*, 1671–1684. [[CrossRef](#)]
96. Hu, B.; Cong, Y.H.; Zhang, B.Y.; Zhang, L.; Shen, Y.; Huang, H. Zhou Enhancement of Thermal and Mechanical Performances of Epoxy Nanocomposite Materials Based on Graphene Oxide Grafted by Liquid Crystalline Monomer with Schiff Base. *J. Mater. Sci.* **2020**, *55*, 3712–3727. [[CrossRef](#)]
97. Padmajan Sasikala, S.; Lim, J.; Kim, I.H.; Jung, H.J.; Yun, T.; Han, T.H.; Kim, S.O. Graphene Oxide Liquid Crystals: A Frontier 2D Soft Material for Graphene-Based Functional Materials. *Chem. Soc. Rev.* **2018**, *47*, 6013–6045. [[CrossRef](#)] [[PubMed](#)]
98. Zhang, Z.; Zhang, J.; Li, S.; Liu, J.; Dong, M.; Li, Y.; Lu, N.; Lei, S.; Tang, J.; Fan, J.; et al. Effect of Graphene Liquid Crystal on Dielectric Properties of Polydimethylsiloxane Nanocomposites. *Compos. Part B Eng.* **2019**, *176*, 107338. [[CrossRef](#)]
99. Solodov, A.N.; Balkaev, D.A.; Shayimova, J.R.; Vakhitov, I.R.; Gataullina, R.M.; Sukhov, A.V.; Burilova, E.A.; Amirova, L.M.; Zhuravleva, Y.I.; Amirov, R.R. Tribological Properties of an Epoxy Polymer Containing a Magnetically Oriented Graphene Oxide/Iron Oxide Nanoparticle Composite. *Diam. Relat. Mater.* **2023**, *138*, 110211. [[CrossRef](#)]
100. Solodov, A.N.; Balkaev, D.; Amirov, R.; Gataullina, R.; Nurtdinova, L.; Yusupov, R.; Kharintsev, S.S.; Dimiev, A.M. Polymer Composites with Magnetically Tunable Optical Anisotropy. *ACS Appl. Polym. Mater.* **2023**, *5*, 6338–6345. [[CrossRef](#)]
101. Bao, T.; Wang, Z.; Zhao, Y.; Wang, Y.; Yi, X. Friction and Mechanical Properties of Amino-Treated Graphene-Filled Epoxy Composites: Modification Conditions and Filler Content. *RSC Adv.* **2020**, *10*, 26646–26657. [[CrossRef](#)]
102. Wu, H.; Liu, C.; Cheng, L.; Yu, Y.; Zhao, H.; Wang, L. Enhancing the Mechanical and Tribological Properties of Epoxy Composites: Via Incorporation of Reactive Bio-Based Epoxy Functionalized Graphene Oxide. *RSC Adv.* **2020**, *10*, 40148–40156. [[CrossRef](#)]

103. Zheng, Z.; Xu, H.; Wen, J.; Chen, J.F.; Mao, Z.; Zhu, P.; Sun, R.; Wu, W.; Peng, J. In-Situ Growth of Diamond/Ag as Hybrid Filler for Enhancing Thermal Conductivity of Liquid Crystal Epoxy. *Diam. Relat. Mater.* **2024**, *141*, 110659. [[CrossRef](#)]
104. Khan, M.; Khurram, A.A.; Tiehu, L.; Zhao, T.K.; Xiong, C.; Ali, Z.; Ali, N.; Ullah, A. Reinforcement Effect of Acid Modified Nanodiamond in Epoxy Matrix for Enhanced Mechanical and Electromagnetic Properties. *Diam. Relat. Mater.* **2017**, *78*, 58–66. [[CrossRef](#)]
105. Khan, M.; Hamid, A.; Tiehu, L.; Zada, A.; Attique, F.; Ahmad, N.; Ullah, A.; Hayat, A.; Mahmood, I.; Hussain, A.; et al. Surface Optimization of Detonation Nanodiamonds for the Enhanced Mechanical Properties of Polymer/Nanodiamond Composites. *Diam. Relat. Mater.* **2020**, *107*, 107897. [[CrossRef](#)]
106. Zhang, Y.; Park, M.; Park, S.J. Implication of Thermally Conductive Nanodiamond-Interspersed Graphite Nanoplatelet Hybrids in Thermoset Composites with Superior Thermal Management Capability. *Sci. Rep.* **2019**, *9*, 2893. [[CrossRef](#)] [[PubMed](#)]
107. Feng, Z.; Liu, X.; Zhang, W.; Zeng, J.; Liu, J.; Chen, B.; Lin, J.; Tan, L.; Liang, L. Functionalized Mesoporous Silica Liquid Crystal Epoxy Resin Composite: An Ideal Low-Dielectric Hydrophobic Material. *J. Mater. Sci.* **2022**, *57*, 1156–1173. [[CrossRef](#)]
108. Qin, T.F.; Wang, H.; He, J.; Qu, Q.Q.; Da, Y.S.; Tian, X.Y. Amino Multi-Walled Carbon Nanotubes Further Improve the Thermal Conductivity of Boron Nitride/Liquid Crystal Epoxy Resin Composites. *Express Polym. Lett.* **2020**, *14*, 1169–1179. [[CrossRef](#)]
109. Tian, K.; Yang, S.; Niu, J.; Wang, H. Enhanced Thermal Conductivity and Mechanical Toughness of the Epoxy Resin by Incorporation of Mesogens without Nanofillers. *IEEE Access* **2021**, *9*, 31575–31580. [[CrossRef](#)]
110. Chen, G.; Hu, J.; Xu, J.; Sun, J.; Xiao, J.; Zhang, L.; Wang, X.; Hu, W.; Yang, H. Liquid Crystalline Composite Stabilized by Epoxy Polymer with Boscage-Like Morphology for Energy-Efficient Smart Windows with High Stability. *Macromol. Mater. Eng.* **2022**, *307*, 2100991. [[CrossRef](#)]
111. Li, H.; Zhang, B.; Yu, K.; Yuan, C.; Zhou, C.; Dunn, M.L.; Qi, H.J.; Shi, Q.; Wei, Q.H.; Liu, J.; et al. Influence of Treating Parameters on Thermomechanical Properties of Recycled Epoxy-Acid Vitrimers. *Soft Matter* **2020**, *16*, 1668–1677. [[CrossRef](#)]
112. Denissen, W.; Winne, J.M.; Du Prez, F.E. Vitrimers: Permanent Organic Networks with Glass-like Fluidity. *Chem. Sci.* **2016**, *7*, 30–38. [[CrossRef](#)]
113. Trinh, T.E.; Ku, K.; Yeo, H. Reprocessable and Chemically Recyclable Hard Vitrimers Based on Liquid-Crystalline Epoxides. *Adv. Mater.* **2023**, *35*, 2209912. [[CrossRef](#)] [[PubMed](#)]

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