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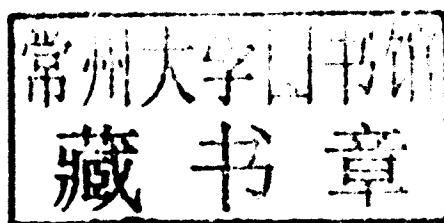
ADHESIVE PROPERTIES IN NANOMATERIALS, COMPOSITES AND FILMS

*Keri A. Wilkinson
Daniel A. Ordóñez*
Editors

NOVA

MATERIALS SCIENCE AND TECHNOLOGIES

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IN NANOMATERIALS,
COMPOSITES AND FILMS**



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PREFACE

This new book examines the adhesive properties in nanomaterials, composites and films. Topics discussed include the properties and applications of composite materials made of Norland Optical Adhesive and liquid crystal materials; adhesive bonding of hydro-thermally modified wood; the use of adhesive films in transdermal and mucoadhesive dosage forms and the durability of adhesives and matrices for polymer composites used in the restoration and rehabilitation of building structures under natural and accelerated weathering conditions.

Chapter 1 - This chapter reviews properties and applications of composite materials made of Norland Optical Adhesive and liquid crystal materials. The polymer support exhibits the texture of a film with Swiss cheese morphology and microscopic inclusions filled with small functional liquid crystal molecules. Under certain conditions of preparation, these systems have a grating morphology with a succession of liquid crystal and polymer shells. Systems with Swiss cheese morphology and mean diameter of inclusions in the micrometer range are strong scatterers of visible light and their applications are mainly in technologies using commutable windows and display devices. Other applications are also possible in multiplexing devices and routing of telecommunication signals provided that the nature of constituents in the initial mixture and the method of preparation are properly chosen. In general, one seeks liquid crystal domains with sizes in the nanometer range either with randomly distributed inclusions or using grating morphology. This study presents a state of the art of the properties of such composite materials encompassing morphology, phase behavior, thermo-mechanical and visco-elasticity aspects. Optical and electro-optical responses which are the basis for numerous applications are also examined. Both theoretical models and experimental investigations will be considered with a special reference to the work with which the authors are most familiar. A correlative analysis is made to demonstrate the relationship between composition of the initial mixture, conditions and methods of preparation and final properties of the materials.

Chapter 2 - Bonded joints made with polymeric matrix composites are commonly adopted in structural applications where weight is a critical design parameter. They are also key elements in the repair and retrofitting of damaged structures, e.g. aircraft composite skin and reinforced concrete bridge columns. Advances in the design and inspection of bonded polymeric composite joints will therefore improve joints durability, and consequently the safety of composite structures, in a wide range of applications (aerospace, civil, ship, transportation and wind power engineering).

The scope of this chapter is to discuss one aspect of joint durability: chemical and mechanical degradation of the individual components of a typical aerospace joint, i.e.

structural epoxy-based adhesive and carbon/epoxy. In a recent research project, these materials were separately exposed to an aggressive environment, consisting of full immersion in water or anti-icing additive (also called fuel additive) or jet fuel or hydraulic fluid. There were simplified laboratory testing conditions: no coatings, no mixing of fluids (i.e. jet fuel and anti-icing additive), no prior thermo-mechanical damage. Gravimetric data, hardness tests and microscopy support the presence of chemical degradation in the adhesive. The use of simple Fickian and non-Fickian two-stage sorption Langmuir models for gravimetric data appears successful for the results of some treatments, e.g. sorption of fuel additive by adhesive. This finding could be used for the purpose of multiphysics modeling of thermo-mechanical degradation of bonded joints. Finally, chemical degradation distinctly appears through Differential Scanning Calorimetry (DSC) and thermogravimetric (TGA) tests: significant changes were encountered when the adhesive was treated in anti-icing additive or hydraulic fluid, while other treatments seem to be much less detrimental for the adhesive. Carbon/epoxy, on the other hand, is impacted at a much lesser rate by fuel additive.

Chapter 3 - The coating of polymer materials by protecting and functional films requires high efforts in the development of coating techniques due to the very different mechanical and thermal properties of polymer substrates and metal or ceramic films. The film has to fulfil both high adhesion and optimized microstructure to prevent failing in its application. The current work describes a new vacuum coating technique for polymer materials with inorganic films – the Pulsed Laser Deposition (PLD) process, characterized by a high-energetic pulsed plasma and the easy possibility to room temperature deposition (RT-PLD). Thus, pseudodiffusion interfaces were found due to the high-energetic particle bombardment during PLD coating. Additionally, changes of the polyurethane chemical binding are evident, like the transition from C=O to C–O–R binding, in which titanium atoms could act as new binding partners to the O species. Although very high film adhesion can be guaranteed in the PLD by the formation of pseudodiffusion interfaces, preventing the well-known buckling phenomenon, high film stresses result in plastic deformation of the soft polymer surface and the formation of wrinkles. The reasons and effects of wrinkling – even starting in growing films – on the film behaviour are described in this work, based on both practical investigations, using transmission electron microscopy, X-ray diffraction and atomic force microscopy, and theoretical finite element modelling.

Chapter 4 - In the past years considerable increase in the hydrothermal modification of wood was observed. Mostly the heat treatments are performed to change the hygroscopicity of wood. Furthermore, densification processes are utilizing the hydrothermal treatments. A key factor in the efficient utilization of timber resources is the adhesive bonding of wood, since manufacturing of wood based composites depends on forming bonds between individual wooden elements. Wood-based composites offer several advantages over sawn wood, such as the utilization of waste material, better distribution of non-homogeneities, and control of the product properties in the manufacturing process. Therefore the efficient utilization of hydro-thermally modified wood depends on its adhesive potential. The combined effects of temperature and moisture modify the properties of the polymeric components of wood and its porous structure. Wood tissue is exposed to high temperatures that can cause surface inactivation. Hydrothermal treatment could reduce the surface free energy and thus result in the poorer wettability of the modified wood surface. Furthermore, penetration and spreading of the resin could be influenced by hydrothermal treatment. In spite of numerous studies of hydro-thermally modified wood, the adhesion potential of hydro-

thermal treated wood has not been studied extensively in the past. The aim of this chapter is to provide literature review of aspects like surface properties of hydro-thermally modified wood related to bondability, wetting, and penetration. Finally, future directions regarding efficient application of hydro-thermally modified wood including densified wood in polymer composites are discussed.

Chapter 5 - Thin polymeric films with adhesive ability are useful for transdermal and mucoadhesive drug delivery systems. Polymer materials with adhesive ability in their dry state are integral to the formulation of patch systems for topical and transdermal drug delivery. Such polymers are often called “pressure sensitive adhesives” due to their capacity to attach to the skin surface with the application of light pressure. In the drug-in-adhesive design the drug is mixed with the adhesive polymer to produce a thin medicated film. The adhesive performance of these films can be monitored directly using tack and peel tests and indirectly by correlation with rheological parameters. Polymers with adhesive ability following absorption of moisture are useful in the formulation of mucoadhesive films for transmucosal (e.g. buccal, nasal, ocular) drug delivery. Such polymers are hydrophilic (hydrogels). Following hydration, polymer chains relax and interact with mucus glucoprotein chains, primarily by hydrogen bonding. This chapter will describe the properties of the adhesive polymers used in the design of transdermal and mucoadhesive films, the mechanism of adhesion and the tests that can be applied to monitor the adhesive performance.

Chapter 6 - In this chapter, a review of theoretical and numerical asymptotic studies on thin adhesive layers is proposed. A general mathematical method is presented for modelling the mechanical behavior of bonding and interfaces. This method is based on a simple idea that the adhesive film is supposed to be very thin; the mechanical problem depends strongly on the thinness of the adhesive. It is quite natural, mathematically and mechanically, to consider the limit problem, that is, the asymptotic problem obtained when the thickness and, possibly, the mechanical characteristics of the adhesive thin layer tend to zero. This asymptotic analysis leads to a limit problem with a mechanical constraint on the surface, to which the layer shrinks. The formulation of the limit problem includes the mechanical and geometrical properties of the layer. This limit problem is usually easier to solve numerically by using finite elements software. Theoretical results (i.e. limit problems) can be usually obtained by using at least four mathematical techniques: gamma-convergence, variational analysis, asymptotic expansions and numerical studies. In the chapter, some examples will be presented: comparable rigidity between the adhesive and the adherents, soft interfaces, adhesive governed by a non convex energy and imperfect adhesion between adhesive and adherents. Some numerical examples will also be given and, finally, an example of a numerical algorithm will be presented.

Chapter 7 - The success of the fiber-reinforced polymer (FRP) systems in the restoration and rehabilitation of civil and monumental structures is due to their excellent properties, generally superior than those of traditional building materials. Of great importance, however, is the behavior of the repaired structure under loading and its durability in the outside climate. The lack of specific standards for durability investigation of materials employed in such applications makes difficult the assessment of reliable theoretical models. As an example, the available standard tests for adhesives generally refer to resins cured at elevated temperatures, neglecting the peculiarities of “cold-cured” adhesives.

In this chapter, the durability of the base components of FRP specifically designed for civil engineering industry, is reviewed. The most common environmental agents, mostly

responsible for the deterioration of the materials performance, are examined. Finally, standardized accelerating tests are discussed as an effective method to predict the long term behavior of the weathered materials.

Chapter 8 - Adhesives or bonding agents surround all living beings in Nature and in their daily lives. Adhesives or bonding agents are used in a variety of industries: construction, packaging, furniture, automotive, appliance, textile, aircraft, and many others. However, most of them are toxic for human beings due to the presence of harmful synthetic additives. The long-term exposure to these toxic substances can cause a range of ailments, including cancer, asthma, and Alzheimer disease. The ultimate solution of this trend lies in the emulation of Nature following the true pathway of natural process. In this paper, a number of adhesives have been formulated from natural additives, which can lead us towards sustainable lifestyles. Experiments show that the product exhibit durability and strength comparable to commercially available products, while the required concentration of the adhesive is low. Further experiments indicate that alternative adhesives that are of organic origin can eliminate the use of synthetic adhesives entirely. Similarly, as a natural alternative to Plaster of Paris is proposed. This product has features very similar to the commercial Plaster of Paris. This product and others can become useful for people with chemical sensitivity, particularly the children and the elderly. This paper describes in detail the specific recommendations on natural adhesives, their strengths and durability as a function of temperature.

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Chapter 1

NORLAND OPTICAL ADHESIVE AND LIQUID CRYSTAL COMPOSITE MATERIALS

Réda Benmouna* and Mustapha Benmouna

University Aboubekr Belkaid, Faculty of Sciences,
Department of Physics, Tlemcen BP119, Algeria.

ABSTRACT

This chapter reviews properties and applications of composite materials made of Norland Optical Adhesive and liquid crystal materials. The polymer support exhibits the texture of a film with Swiss cheese morphology and microscopic inclusions filled with small functional liquid crystal molecules. Under certain conditions of preparation, these systems have a grating morphology with a succession of liquid crystal and polymer shells. Systems with Swiss cheese morphology and mean diameter of inclusions in the micrometer range are strong scatterers of visible light and their applications are mainly in technologies using commutable windows and display devices. Other applications are also possible in multiplexing devices and routing of telecommunication signals provided that the nature of constituents in the initial mixture and the method of preparation are properly chosen. In general, one seeks liquid crystal domains with sizes in the nanometer range either with randomly distributed inclusions or using grating morphology. This study presents a state of the art of the properties of such composite materials encompassing morphology, phase behavior, thermo-mechanical and visco-elasticity aspects. Optical and electro-optical responses which are the basis for numerous applications are also examined. Both theoretical models and experimental investigations will be considered with a special reference to the work with which the authors are most familiar. A correlative analysis is made to demonstrate the relationship between composition of the initial mixture, conditions and methods of preparation and final properties of the materials.

* E-mail: redabenmouna@yahoo.com

1. INTRODUCTION

Norland Optical Adhesive in short NOA is a commercial product made essentially of a mixture of mercapto-ester with acrylate monomer. Its precise composition is not disclosed in the open literature but with the information available, it is possible to construct its molecular structure. It contains in addition to benzophenone, the 3 types of monomers: trimethylolpropane diallyl ether, trimethylolpropane trithiol and isophorone di isocyanate ester. [1,2] The photo-initiator benzophenone which is present at a known concentration is very efficient and has a high absorption cross section in the UV-visible and IR spectrum. Different types of adhesives may be encountered depending on composition and dedicated applications. NOA65 is among the most used ones in fundamental studies. It is an efficient non toxic adhesive with a capacity to form densely cross-linked networks under UV curing. Thiol radicals present in NOA65 contain sulfur groups (-SH) that allow polymerization under ordinary atmospheric environment without the inhibition by O_2 often encountered in the chemistry of unsaturated polyesters and acrylates. Its curing kinetics is much less sensitive to material mass than other hardeners and can be used in thin film cures.

Cure time depends upon dose, intensity and wavelength. The radicals initiate a cascade of polymerization reactions in the presence of monomers with double bonded vinyl groups. At a certain time, a phase separation mechanism takes place. While the polymerization is initiated by production of free radicals via radiation exposure, the phase separation mechanism is governed by combined changes in the system composition and its solubility properties. At final stages of polymerization, the system transforms into a more or less hard solid consisting of a cross-linked polymer network.

UV photo-polymerization of NOA is used in a variety of high performance coating for vinyl or wood flooring, metal and wood furniture, printing plastics, paper packaging, circuit board coating, and metal containers.[3-5]

Mixing such a solid material with a low molecular weight liquid crystal yields thin films that can be used as a support in photonic devices, microelectronic assemblies and hybrid organic – inorganic compounds. Such technologies are nowadays under constant development for many applications including display and telecommunications devices.[6-8]

In view of their importance both from the fundamental and applications standpoints, it would be useful to examine the properties of these compounds in order to advance our understanding on their specific behavior and elucidate some of their intriguing properties. The present work is a contribution along these lines scrutinizing different properties directly related with applications.

This chapter is organized as follows. In the first section we discuss the method of film preparation and morphology development. A strong correlation exists between composition of initial mixture, conditions of preparation and properties of the synthesized product. A special focus is put on the photo-curing process via Polymerization Induced Phase Separation (in short PIPS). The fundamental properties are intimately related with the final morphology and morphology development in the course of film preparation. The type of application is often conditioned by morphology considerations. The phase behavior, thermo-physical, thermo-mechanical and visco-elastic properties are the subject of sections 2 and 3. Evolution of the phase diagram from the initial state to the final cured film retains a particular attention. Transition temperatures of major events characterizing the system may be examined using a

variety of techniques. The mechanical tenure and visco-elasticity of films subject to repetitive use under extreme conditions bear a strong impact on their performances and ageing and should be analyzed carefully. These aspects are also examined. Questions related with optical and electro-optical properties are at the basis of most applications in a variety of domains leading to new routes of development in modern technologies. These are the subject of section 4. Conclusion gives a brief synthesis of results.

2. POLYMERIZATION INDUCED PHASE SEPARATION AND MORPHOLOGY DEVELOPMENT

2.1. Polymerization Induced Phase Separation

There are at least two main routes for fabricating polymer and liquid crystal composites materials. One consists of mixing together the pre-polymer and liquid crystal in the presence of a compatibilizer. This is the common way taken to obtain polymer dispersed liquid crystal films for privacy windows at the industrial level. Since the polymer and liquid crystal are not miscible under normal atmospheric conditions the compatibilizer which consists of water and an emulsifier (Sodium Dodecyl Sulfate in short SDS) is added to obtain a miscible system. After reaching the equilibrium state of a completely mixed system, the solvent is evaporated to obtain a film with Swiss cheese morphology whereby liquid crystal molecules are confined in the polymer pores. [9,10] The second route is the one that retain our attention in this chapter since it is commonly used to investigate the fundamental aspects of such multi-component mixtures. It consists of adding monomer and liquid crystal prior to polymerization and is referred to as Polymerization Induced Phase Separation. It leads to a variety of interesting properties for fundamental studies as we shall demonstrate throughout different parts of this chapter.[11,12]

Interplay between kinetics of polymerization and phase separation in polymer and liquid crystal materials is dominated primarily by the increasing molar weight and gelation mechanism of the polymer network. Elastic forces at the polymer and liquid crystal interface play a key role in the morphology development and performances of the film. [13]

The phase separation mechanism starts with nucleation of liquid crystal domains driven by monomer reaction kinetics. As this process evolves, nematic domains grow via Oswald ripening and diffusion mechanisms until completion of monomer consumption. [14] The final state exhibits a characteristic swiss cheese morphology with pores filled with small liquid crystal molecules distributed throughout the polymer network.

A low curing intensity leads to slow kinetics of polymerization and large liquid crystal domains. The lower is the rate of polymerization, the larger the size of these domains. Under such conditions, the composite is characterized by a high level of scattering in the visible range which is perfectly suitable for display devices. [15,16] Conversely, using high intensity curing sources speeds up the polymerization kinetics shifting the size to the submicron or even the nanometer range. At a certain stage of the polymerization kinetics, solvent molecules may exhibit a poor solvation with respect to the growing polymer while monomer exhibits a higher miscibility, then nuclei coalesce to form large aggregates separated by inclusions filled with liquid crystal molecules. If the polymerization rate is fast, the transition to a network

polymer is accelerated leading to nano sized droplets distributed throughout the volume. On the other hand, a high intensity source may lead to poor phase separated not uniformly distributed inclusions with diameters ranging from say 200 to 650nm. Low intensity sources yield nearly spherical domains in the micrometer range, well distributed throughout the volume. Small inclusions are found near the surface directly exposed to the source. [17] During curing the temperature rises faster for higher source intensity. The rate of nucleation and growth of liquid crystal domains depends on activation energies of nucleation and diffusion. There is a subtle interplay between these activation processes especially in terms of temperature and radiation dose. Viscosity of the medium plays a determinant role in favoring one or the other process.[18]

From the theoretical point of view, one has to solve coupled equations for the polymerization kinetics and dynamics of phase separation. To this end, Cahn-Hilliard-Cook theory of spinodal decomposition is often combined with other theories such as Flory-Huggins lattice model to develop a formalism of phase separation and kinetics of polymerization. These models involve parameters related with the mobility of molecules within the systems together with interfacial parameters characterizing the degree of incompatibility between unlike species.[19-22] Important quantities such as diffusion coefficients and rate constants of polymerization should be properly incorporated in the model to solve the problem.[23] Note that curing radiation and polymerization induce substantial heating within and beyond the exposed region because of diffusion mechanism and this should be taken into consideration in modeling these processes.[24, 25]

2.2. Morphology Development

Morphology is the prerequisite to any investigation because it determines to a large extent the performance under practical conditions of applications. It is intimately related with the nature and composition of the initial mixture as well as with the conditions of preparation. The size of inclusions is within μm or nm and keeps increasing with the amount of liquid crystal. Similar trends are also found by fixing the latter quantity and lowering the temperature below the isotropic to nematic transition. Competing processes of polymerization and phase separation and their respective kinetics can be monitored to obtain one or the other of the following composites: Phase separated composites films [26], PDLCs [27] and Holographic PDLCs [28] are shown in figures 1 a, b and c, respectively.

In the first case, curing radiation penetrates the sample with an intensity gradient and the exposed side undergoes fast polymerization with significant space and time modulations. This leads to two distinct domains as shown in panel (a). The polymer film is formed on the exposed side while the back side which receives a lower intensity is mainly made of liquid crystal molecules. Polymer Dispersed Liquid Crystal (Panel b) consists of a Swiss cheese morphology whereby the liquid crystal phase is dispersed in the polymer matrix in the form of inclusions. Depending on the preparation conditions, in the course of polymerization and phase separation processes, a variety of mesoscopic structures emerge. The growing molecular weight of network generates elastic stresses that bear strong effects on morphology developments. Diffusion and coalescence phenomena, nematic, smectic or higher order structures have to be taken into account to describe these developments characterizing the phase separated composite material. [29] Optical microscopy is sufficient to resolve particle

size distribution in the micron range whereas for nano structured systems a more appropriate observation technique should be considered based on electron or atomic force microscopy. In this case, a careful preparation of samples is necessary to enhance the contrast conditions together with powerful software to analyze size distributions. [30, 31]

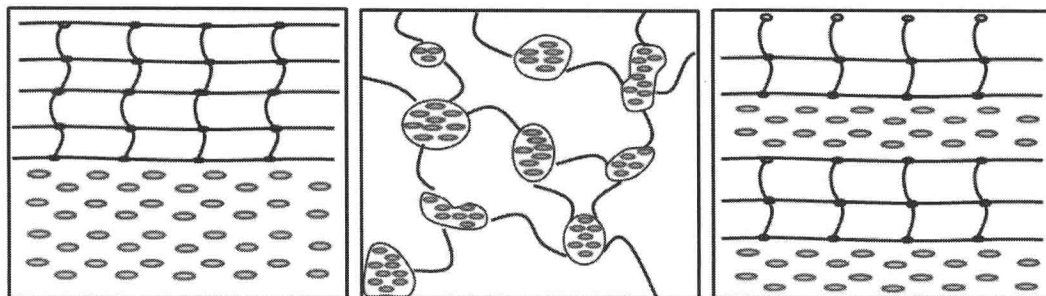


Figure 1. Schematic representation of (a) Phase Separated Composite films (b) Polymer Dispersed Liquid Crystals (c) Holographic Polymer Dispersed Liquid Crystal.

Specific morphologies are chosen according to the needs in terms of practical applications. A major effort is currently put on polymer dispersed liquid crystals with grating. These systems consist of arrays of liquid crystal and polymer thin layers with nano dimensions. [31] These arrays are built by implementing a procedure of preparation based on interferences between two laser beams. Such approach is suitable for systems like fiber optics, telecommunication routing and multiplexing, spectral selectivity and light valves with multiple wavelengths. [32] Photo-polymerization Induced Phase Separation mechanism may be used to achieve systems with random dispersions of nano-sized spherical domains filled with small liquid crystal molecules. These are characterized by an orientation order along a director axis. Orientation distribution throughout the polymer matrix is random in the quiescent state but may change when activated by an external field. These systems offer wide prospects in terms of applications comparable to systems exhibiting grating morphology of nano domains but their fabrication is much simpler. [33, 34]

Panel (a) of figure 2 shows the morphology developments upon cooling of the uncured NOE65/E7 system at a concentration of 70wt%E7. A transition from a single phase isotropic liquid to a biphasic system exhibiting a nematic structure is clearly seen. Another path was envisioned as illustrated in panel (b) of this figure where temperature was fixed and content of liquid crystal increased. On the left hand side, one observes a single phase of an isotropic liquid. When the amount of E7 increased, a nematic phase emerged with an increasing number of domains as one enters deeply into the biphasic region.

Figure 3 a, b, c show typical images obtained by Scanning Electron Microscope (SEM) of NOA65/E7 cured systems. These images are accompanied by histograms describing the pore size distribution within the polymer matrix. These are typical examples of morphology developments. Detailed investigations of pertinent parameters affecting the morphology of thiolene systems like these were reported elsewhere. [33-36] As the concentration of liquid crystal increases, pore size increases approaching the micrometer range. Porosity of the medium can be roughly estimated by the concentration of porogen which, in the present case is the low molecular weight liquid crystal.

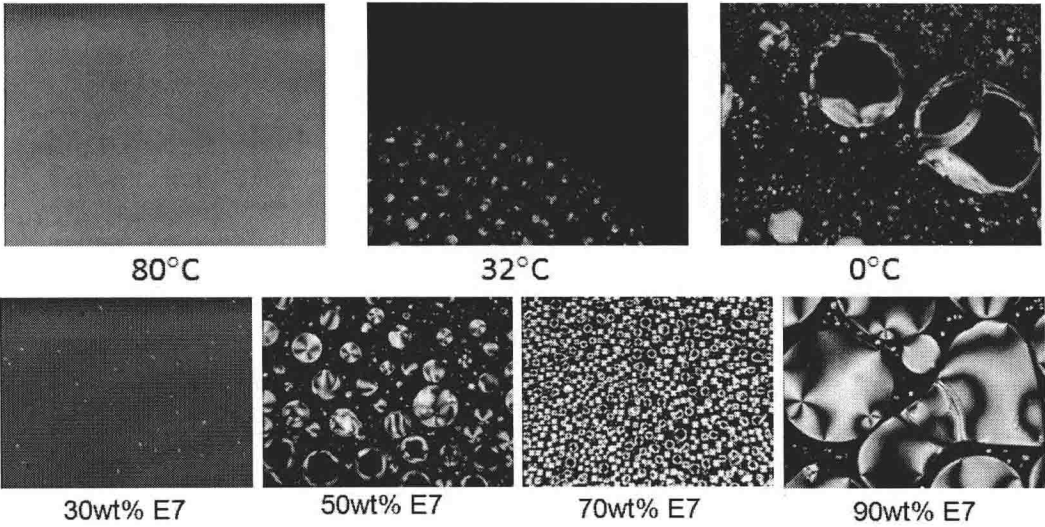


Figure 2. Morphology development of the uncured NOA65/E7 as obtained by Polarized Optical Microscopy (a) Upon cooling the mixture with 70wt% E7 (The corresponding temperature are indicated) (b) Increasing the content of E7 at 20°C (The concentration of E7 are specified on the figure).

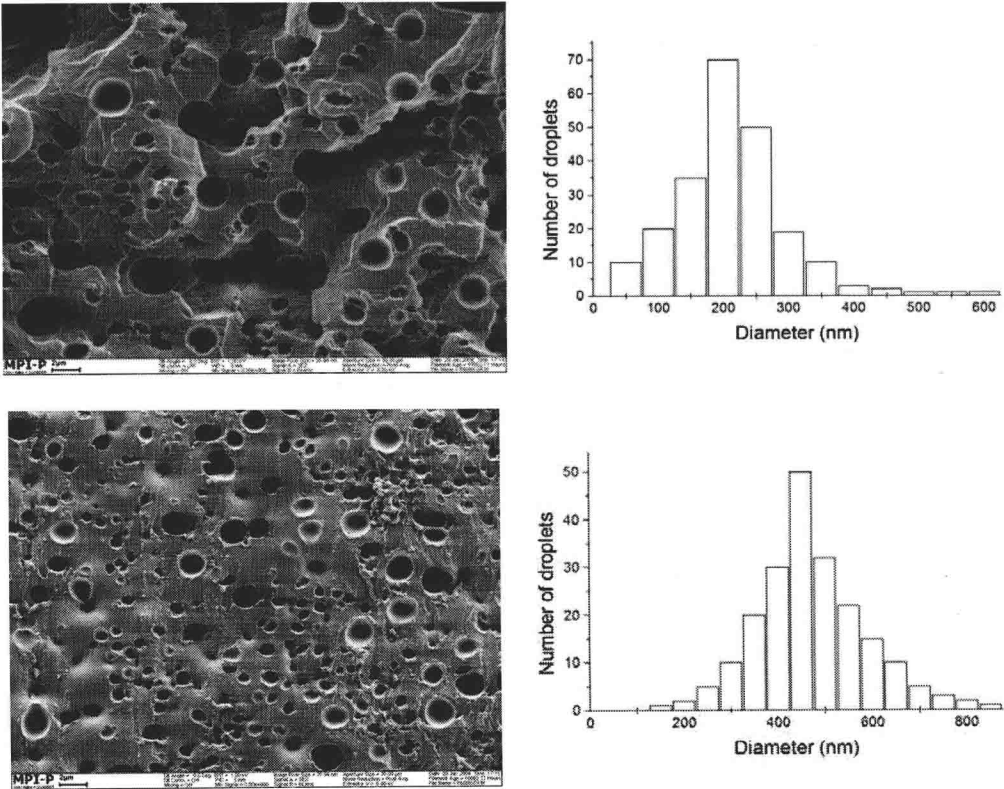


Figure 3. (continued).

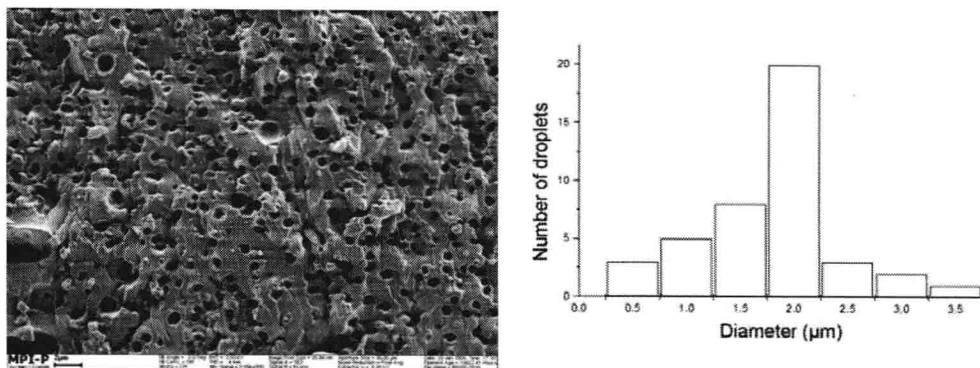


Figure 3. Morphology development of the cured NOA65/E7 system as obtained by Scanning Electron Microscopy (a) Micrograph and corresponding histogram at 35wt% E7 (b) 30wt% E7 (c) 25wt% E7.

A large increase in the pore size is not particularly suitable because of the scattering enhancement of visible light which could alter system efficiency. Conditions of photopolymerization should be controlled with care since the dose of curing radiation, the nature and concentration of initiator and cross-linker should be chosen carefully to achieve the right system for the desired application. Higher functionality or concentration of cross-linker yield densely cross-linked polymer networks promoting the formation of smaller pores with the risks of generating heterogeneities.

For multiplexing devices, one would need a system with randomly dispersed nano-pores where the low molecular weight molecules remain totally confined. The amount of liquid crystal dispersed in the polymer matrix should be reduced for several reasons. Practical uses of these devices articulate around the ability of the liquid crystal molecules to respond properly and promptly to signal commands. Optimal conditions of the sensing behavior are achieved if all the LC molecules are fully confined in the pores. A way to control this situation is to measure the enthalpy exchange at the nematic to isotropic transition which, according to the method of Smith [37], gives the amount of molecules confined in pores. Small molecules dispersed in the supporting medium act as a plasticizer lowering its T_g with negative consequences on mechanical strength, ageing and performances.

Admitting that porosity is given by the porogen concentration, namely

$$\text{Porosity} = \frac{V_{\text{pores}}}{V_{\text{total}}} = \frac{\pi D^3 (\text{number pores})}{6 V_{\text{total}}} = \phi_{\text{LC}}, \text{ one finds that the mean diameter of pores}$$

should scale like $\phi_{\text{LC}}^{1/3}$ which is in discrepancy with the experimental finding of references [33, 34] where D was found to be proportional to ϕ_{LC} . Such difference could be attributed to a lack of sufficient experimental data since only 3 measurements were reported and polydispersity may hide the real power law between ϕ_{LC} and D besides the fact that porosity should take into account the unavoidable amount of molecules that remain in the polymer matrix.

Obviously, the properties of these materials are highly sensitive to the quality of initial uncured systems. Aimed properties and applications correlate directly to the initial composition and temperature. This is why the phase diagram in the temperature composition

frame is of primary importance to push for further investigations of the properties of polymer and liquid crystal composites.

3. PHASE BEHAVIOR AND THERMOPHYSICAL PROPERTIES

3.1. Phase Behavior

The experimental phase behavior of low molecular weight liquid crystal and polymer systems can be rationalized using simple mean field theories combining the Flory-Huggins [38] lattice model for isotropic mixing and the Maier-Saupe [39] model for nematic order. This combination is appropriate to the initial uncured solution and to cured films involving linear polymers. Therefore, it would be useful to recall the main steps for the derivation of the phase diagram starting from the free energy. This can be written as a sum of the isotropic Flory-Huggins free energy density and the nematic Maier-Saupe contribution. We have

$$\frac{f_{FH}}{k_B T} = \frac{\phi_1}{N_1} \ln \phi_1 + \frac{\phi_2}{N_2} \ln \phi_2 + \chi \phi_1 \phi_2 \quad (1)$$

where ϕ_1 and ϕ_2 are volume fractions of liquid crystal and monomer, N_1 and N_2 their respective numbers of repeat units and χ is the Flory interaction parameter. We shall assume in the case of uncured systems that $N_1 = N_2 = 1$ together with the incompressibility condition $\phi_1 + \phi_2 = 1$. The interaction parameter varies with temperature according to the common form

$$\chi = A + \frac{B}{T} \text{ where } A \text{ and } B \text{ are constants independent of temperature.}$$

Orientation nematic order is described by the Maier-Saupe free energy expressed in term of the order parameter S and the partition function Z .

$$\frac{g_{MS}}{k_B T} = \frac{1}{N_1} \left[-\phi_1 \ln Z + \frac{1}{2} v \phi_1^2 S^2 \right] \quad (2)$$

The order parameter is given by

$$S = \frac{1}{2} \left[3 \langle \cos^2 \theta \rangle - 1 \right] \quad (3)$$

where θ is the angle between a reference axis and the director while the symbol $\langle \dots \rangle$ represents an average with respect to the angular distribution. The nematic partition function reads

$$Z = \int d(\cos \theta) \exp \left[-\frac{m}{2} (3 \cos^2 \theta - 1) \right] \quad (4)$$