Overview

Thermal and extensive rheological investigations have been carried out on nematic liquid crystal gels prepared by gelating a room temperature nematic liquid crystal and a novel dipeptide-based organogelator, the latter being a chiral liquid crystalline compound. For certain concentrations, the calorimetric data display a two-peak profile across the isotropic to chiral nematic transition, a feature reminiscent of the random-dilution to random-field cross-over observed in liquid crystal-aerosil composites. All samples show shear-thinning behaviour without a Newtonian plateau at low shear rates. Dynamic rheological measurements establish the elastic nature of the gels. At low angular frequencies gels exhibit a frequency dependence of the storage ($G'$) and loss ($G''$) moduli. At higher frequencies, while lower concentration composites have a strong frequency dependence with a trend for possible cross-over from viscoelastic solid to viscoelastic liquid behaviour, the higher concentration gels show frequency-independent rheograms of entirely elastic nature, i.e., $G' > G''$. The highlight of this work is the observation of soft glass rheological (SGR) behaviour in the NLC gels—commonly seen in materials like foams, slurries, pastes etc. Some of the observed experimental features that reveal the SGR characteristics are as follows: (i) plateau modulus $G'$ is described by a power-law with an exponent value similar to that observed for other soft materials, (ii) beyond a critical strain, strain-softening of the moduli with a peak in $G''$, (iii) power-law variation of $G'$ in the non-linear viscoelastic regime and (iv) absence of Cox-Merz superposition for the complex viscosity.

These results are published in:

2.1. Introduction

In recent times, low molecular weight materials possessing the ability to gelate organic solvents are generating considerable interest in scientific and technological fields [1-14]. Low molecular mass organogelators (LMOG), as these materials are referred to, are capable of forming rigid fibre-network through either covalent or non-covalent interactions. Organogels formed through non-covalent interactions such as hydrogen bonding (H-bonding) forming physical gels, being thermoreversible are more attractive. If the solvent is a liquid crystal, a new dimension of stimuli-response is added to the inherent mechanical rigidity of the gels giving rise to a new class of dynamically functional soft solids known as liquid crystal gels (LC gels). Ever since the pioneering work carried out by Kato and co-workers [5, 6], LC physical organogels have been the focus of extensive research for a wide variety of applications [13-20]. The development of such materials with immense technological potential requires a thorough understanding of the viscoelastic properties of LC gels, especially in the nematic phase. However, very little is known regarding the rheology of nematic liquid crystal (NLC) gels till date, necessitating a systematic study of this field.

Soft materials such as foams, emulsions, pastes, slurries, colloidal gels etc. exhibit similar and interesting rheological properties. The fact that these materials exhibit analogous rheological features is suggestive of a common cause and it has been argued that these features are suggestive of the general presence of a slow, glassy dynamics in such materials [21, 22]. They share characteristics of structural disorder and metastability, i.e., large energy barriers hinder reorganization into states of lower free energy because this would require rearrangement of local structural units, such as droplets in a dense emulsion. Hence the name ‘Soft Glassy Materials’ (SGMs) was proposed to describe such materials. To explain the rheological behaviour of such SGMs, a theoretical model referred to as Soft Glass Rheology (SGR) model, has been developed [21-25]. It is based on Bouchaud’s trap model [26] of
glassy dynamics, with the addition of strain degrees of freedom, and the replacement of the thermodynamic temperature by an effective (noise) temperature.

In this chapter, thermal and extensive rheological investigations have been carried out on NLC-organogels, prepared by gelating a room temperature NLC with a novel dipeptide-based organogelator [27]. The gelator is capable of gelating common organic solvents even when present in low concentrations. An earlier study from the same laboratory showed that a NLC gel formed by doping low concentration of the gelator is mechanically robust and exhibits faster electro-optic switching compared to pure NLC [14]. The present study employs this NLC-dipeptide system covering a wide range of concentrations placing emphasis on the rheological properties.

2.2. Experimental details

The host NLC employed E7 is a well-known commercially available eutectic mixture obtained from Merck showing nematic phase over a wide range of temperature through room temperature. The constituent compounds of E7 and the phase sequence are shown in figure 2.1. The gelating material employed, a monodisperse homomeric dipeptide, referred to as GSC98 hereafter, is an enantiomer in which the first and second residues are derived from D-alanine [27]. It possesses built-in mechanisms for self-assembly, capable of forming intermolecular H-bonding when doped in organic solvents that enables the formation of a 3-D physical network of fibres. Being a chiral molecule, it also exhibits a macroscopic helical structure; in fact, alanine is known to have a high propensity for helix formation. Structurally, GSC98 can be regarded as an intermediate between polycatenars and taper-shaped amphiphiles as it possesses two lipophilic (half-disk shaped) segments interlinked through a peptide unit. This compound is mesogenic exhibiting a columnar phase, and the mesogenicity helps in preparing mixtures with better homogeneity. It is found that even at concentrations
as low as 0.2% (by weight) GSC98 forms gels with E7. The molecular structure as well as the transition temperatures of this material is shown in figure 2.1.

2.2.1 Preparation of gel composites

Different gels of concentrations $X = 0.2, 0.4, 0.6, 0.8, 1, 2, 4, 6, \text{ and } 10$ where $X$ represents the concentration of GSC98 by weight % in E7 have been prepared for this study. The procedure for the preparation of gels is as follows: In small quantities, GSC98 is completely solvable in E7. The required quantities of E7 and GSC98 were weighed in a glass vial. The mixture was heated to $100 \, ^\circ C$ (which is well above the isotropic temperature of E7 and the melting temperature of GSC98) and stirred constantly for homogeneous mixing. The homogeneous mixture was quenched to room temperature and kept under refrigeration for 2 days to achieve gelation. The gels so formed are stored at room temperature for further use.

2.2.2 Experimental techniques

Visual observations of the microscopic textures have been carried out using a polarising optical microscope (Leica DM4500P) equipped with a temperature-controlled hot stage (Mettler FP82HT) on the composites by inserting them between a pair of optically flat glass
substrates. The xerogel was obtained by leaching out the NLC using ethanol. Scanning electron microscope (SEM) images were recorded using NOVA NANOSEM 600 (FEI, The Netherlands). The sample was prepared on a glass substrate as explained in chapter 1. Circular Dichroism (CD) measurements have been carried out using Jasco J-810 Spectropolarimeter. The sample sandwiched between a pair of quartz substrates was gelated in-situ. The CD spectra in the wavelength range of 200 nm to 800 nm were obtained both in the gel and sol states. Differential scanning calorimetry (DSC) measurements have been performed by using Perkin-Elmer Diamond DSC. For this purpose, known quantity of the freshly prepared NLC-gelator mixture while still in the sol state was taken in aluminium DSC cups and gelated in-situ by keeping the sealed cups in refrigerator for two days. Rheological measurements are performed using the AR-G2 rheometer (TA Instruments) by employing parallel plate geometry of 8mm diameter and geometry gap being maintained at 800μm. Temperature of the samples were maintained constant at 25°C by using a built-in Peltier temperature controller. The detailed description of these techniques is presented in chapter 1.

2.3 Results and Discussion

2.3.1 Gel formation

Detailed rheological investigations are required to unambiguously establish the nature of the gel composites. However, on a qualitative level, the formation of a gel can be quickly confirmed from the test tube inversion method [28]. It was indeed seen that at room temperature E7-GSC98 composites did not flow, indicating the formation of gel (figure 2.2(a)) whereas the pure NLC in the nematic phase (N-sol) exhibits a free-flow as shown in figure 2.2(b).
2.3.2 Polarising optical microscopy (POM)

The composites were filled in LC test cells fabricated using glass substrates coated with polyimide layer rubbed unidirectionally to promote planar alignment. Before gelation, the textures observed between crossed polarisers, for low concentration composites (X < 2), showed typical planar nematic patterns. On gelation, the textures (figure 2.3(a, b)) were not very different from that seen in N phase (N-sol) except that the director fluctuations,
commonly seen in NLC were quenched. The gelated nematic phase is termed as N-gel. This is a tool to identify the onset of gelation in low concentration NLC composites wherein the width of fibres are in submicron length scales and are not visible under an optical microscope. In the case of composites with X>2, the un-gelated sol phase exhibits fingerprint textures, typically observed for a chiral nematic or cholesteric phase (figure 2.3(c) for X=4). GSC98 being a chiral molecule induces chirality in nematic phase of the composites, as is evident from the above observations. On gelation, the texture observed at room temperature is shown in figure 2.3(d). The texture consists of a fibre-like growth superimposed on the planar nematic. Even at the highest gel concentration (X=10), no evidence of phase separation was seen in the microscopy observations.

2.3.3 Circular dichroism (CD)

The CD spectrogram obtained in the gel state for X=2 at room temperature shows a very clear CD signal (figure 2.4). On heating the sample to the isotropic phase the intensity of the CD peak disappears completely. The results clearly indicate that the gelator molecules self-assemble to form helically stacked aggregates in the gel state which gets manifested as the

![CD spectra for X=2 showing a peak in the gel phase which is absent in the isotropic (Iso) phase indicating the enhancement of helical structure on gelation.](image-url)
enhanced CD signal. One of the first observations of such an enhancement of CD intensity in an organogel was made by Weiss and co-workers [29] in a system of dodecane and chiral organogelator CAB (cholesteryl 4-(2-anthryloxy)butanoate). A brief review of CD characteristics of gels can be found in ref. [30].

2.3.4 Scanning electron microscopy (SEM)

The SEM image obtained for the xerogel of X=2 is shown in figure 2.5(a). The image is compared with the one obtained (figure 2.5(b)) for the organogel prepared using the same gelator (GSC98) but with ethanol as a solvent [27]. Both the images reveal the occurrence of a 3D network comprising fibres featuring a right-handed twist (more clearly visible in the case of organogel). Such a feature of molecular chirality of organogelators being manifested as nanoscale helicity in the gel fibres is reported in several cases in literature [31-35].

Based on the above observations, especially the CD and SEM data, it may be reasonable to presume that the gel formation is due to the inter-molecular H-bonding of the gelator molecules aided by the helical interactions (figure 2.6(a)). This results in a fibre growth in all directions giving rise to a 3-D network encapsulating the NLC and resulting in gel formation. A schematic representation of the NLC gel is shown in figure 2.6(b). For the sake of simplicity, the helical structure of the macroscopic gel structure is not shown.

Figure 2.5: SEM images of xerogels obtained from (a) NLC gel (X=2) and (b) organogel (from ref. 27) showing the helical twist of the fibres.
2.3.5 Thermal Behaviour

Differential scanning calorimetric (DSC) measurements were carried out in the heating mode (at 5°C/min) for E7 and the composites. The thermograms obtained for the representative concentrations X=1, 2, 4 and 10 are shown in figure 2.7. The composites X=1 and 10 show a single peak corresponding to the isotropic-to-nematic (Iso-N) transition. (Note that in the case of X>2 composites, the mesophase is actually chiral nematic phase. But for the sake of simplicity, it will be referred to as nematic unless it is important to bring in the chiral nature of the phase). All other composites except the composites with intermediate concentration X=2 and 4, exhibit similar single peak. The composites X= 2 and 4 exhibit a profile qualitatively different from the rest. A twin-peak profile is seen for the two composites in the vicinity of the transition. This is reminiscent of the behaviour seen in aerosil-LC composites wherein the LC molecules are confined in a fragile network formed due to the H-bonding between the silica particles of aerosil [36, 37]. An important difference between the network formed in aerosil-LC and the present case of peptide-LC should be mentioned. The origin for both networks is the hydroxyl group- present within the molecule for the peptide case and existing as a terminal group attached to SiO₂ in the case of aerosil particles. Therefore, the interaction between the hydroxyl groups of neighbouring peptide molecules is augmented if
the orientational order is non-zero. Consequently, it will be weakened for small values of orientational order and certainly in the isotropic phase. Since the aerosil particles do not take part in the formation of the LC structure, the strength of H-bonding between neighbouring aerosil particles is not affected by the liquid crystalline order. A noteworthy feature is that it has been established that the aerosil gel system is soft in the concentration range up to 10%, showing soft glass behaviour generally seen for materials such as foams, emulsions, particulate suspensions, and slurries [38].

High-resolution ac calorimetry [39] as well as DSC measurements [36, 37] have shown that for certain concentrations these soft gels exhibit two closely spaced and sharp thermal features, which have been used [40] to propose that the nematic order develops from the isotropic phase through a two-step process and that the double peak in the calorimetry data is due to a cross-over from a random dilution regime, where the silica gel couples to the
scalar part of the nematic order parameter, to a low-temperature random-field regime, where the coupling induces distortions in the director field. Owing to the common feature that in the present case also the gel formation involves a network of H-bonded entities (GSC98 molecules), it will be possible to borrow these ideas to interpret the DSC results. For the quantitative analysis, the data for $X = 2$ and 4 were fit to a sum of two Gaussian expressions. Similar to what has been observed in the aerosil case, the composites exhibit a double peak profile but with a significant difference. Whereas in the aerosil system the temperature difference between the two peaks is always a fraction of a degree, in the present case the peaks are well separated, by as much as 3 °C. This perhaps suggests that even for small values of the nematic orientational order the network gains strength in aerosil systems but requires higher orientational order in the present case. However, as shall be seen later, deeper in the mesophase the network strengths of the two systems, viz., the aerosil and the GSC98 composites, quantified by the storage modulus are comparable. The transition enthalpy $\Delta H$, calculated from the area under the peak, is smaller for the composites, suggesting that the transition becomes weaker in the presence of the quenched disorder. From the double-peak profile of $X = 2$ composite, it is seen that the magnitude of $\Delta H$ corresponding to the high-temperature process, associated with the random dilution limit, is three times larger than the one connected with the random field region, a feature opposite that observed in the case of the aerosil-LC systems.

Based on the POM and DSC observations, it is possible to construct a phase diagram indicating the dependence of Iso-N transition temperature ($T_{NI}$) on the concentration of GSC98 as shown in figure 2.8. The strong decrease in $T_{NI}$ with increasing concentration suggests the structural incompatibility between the host NLC and the guest peptide molecules, with the latter acting as impurities. The salient feature, however, is the presence of the additional peaks in DSC scans for $X = 2$ and 4 composites but absent for the lower and
higher concentrations, indicating that the cross-over mentioned above can be seen only in the soft gel limits.

2.3.6 Rheological characterisation

Steady-state and dynamic rheological measurements have been performed on all the gel composites to determine the viscoelastic behaviour in the gel state. In chapter 1, a summary on the rheology of gels in general and different types of rheological measurements is presented. All the rheological measurements discussed in the following sections have been carried out at room temperature of $T=25 \, ^\circ C$.

Before discussing the results, the salient features of the SGR model proposed by Sollich and co-workers [21-25] are reviewed below. The features of the SGR model is schematically shown in figure 2.9. The model incorporates only those characteristics, namely structural disorder and metastability, deemed common to all SGMs. The macroscopic soft matter is conceptually divided into mesoscopic elements. Each element has local shear strain $\gamma$ which increments with macroscopic shear $\dot{\gamma}$. The strain rate $\dot{\gamma}$ is assumed to be uniform throughout the system but variation in local strain and stress is allowed. When the strain energy given by $\frac{1}{2} k l^2$ (where $k$ is the local modulus) reaches the yield energy $E$, the element yields and $\gamma$ is reset to zero. Note that each element has its own $E$. When an element yields it
Figure 2.9: Each mesoscopic element represented by a polygon yields when it overcomes $E$. The bottom of each trap corresponds to the unstrained state $l = 0$. In straining an element by an amount $l$, the representative particle moves up the sides of the trap. When $E \equiv \frac{1}{2} kl^2$, it can hop by the activated dynamics ($'x'$) to the bottom of another one.

The yielding itself is activated by an effective temperature $'x'$, also known as 'noise temperature' to model the interactions between the elements. $x$ should be the order of $E$, much larger than $k_B T$. Conceptually, $x$ can be interpreted as their actual thermodynamic temperature because the elements are slow to equilibrate and this does not generally coincide with the temperature of fast degrees of freedom or heat bath. The probability of yielding of each element in unit time is dependent on $x$. At $x=1$ (in appropriate units), the glass transition occurs. The exact solution of the model takes the form of a constitutive equation relating stress to strain history, from which all rheological properties can be derived. The predictions of the SGR model, governing the universal behaviour of rheological properties of SGMs, are briefly discussed below.

Within the linear viscoelastic regime (LVR) in oscillatory strain measurements, both the storage ($G'$) and loss ($G''$) moduli vary with the angular frequency ($\omega$) of the applied strain as power law of the following form:

$$G' \sim \omega^{x-1} \text{ and } G'' \sim \omega^{x-1}$$

(2.1)

for $1 < x < 2$. Near the glass transition, the curve defined by this power-law nearly becomes
flat and aging is predicted in the glass phase. In the non-linear viscoelastic regime, as the strain amplitude is increased, the loss modulus ($G''$) passes through a maximum near the glass transition before decreasing. Large strain amplitude shows fluidization of the moduli, which is similar to experimental observations. The steady shear flow curves show shear-thinning behaviour. For $x < 2$, power-law fluid behaviour, with a non-zero yield stress in the glass phase is seen. Further, the Cox-Merz rule fails in this non-Newtonian regime according to this model.

2.3.6.1 Steady state measurements

Steady state measurements were carried out on the ‘as loaded’ composites by monitoring the shear viscosity ($\eta$) as a function of the shear rate ($\dot{\gamma}$). The flow curves obtained are shown in figure 2.10 for gels with concentrations ranging over two decades and shear rates ($\dot{\gamma}$) over nearly six decades. All composites exhibit shear-thinning behaviour of viscosity $\eta$ at shear rates in the range of $\dot{\gamma} = 3 \times 10^{-3}$ s$^{-1}$ to 0.8 s$^{-1}$. The shear-thinning behaviour is a trait

![Figure 2.10](image)

**Figure 2.10**: Shear rate ($\dot{\gamma}$) dependence of effective viscosity ($\eta$) for different concentrations of the composite. Shear thinning and the absence of low shear-rate Newtonian plateau is clearly observed.
exhibited by most soft glassy materials. An essential feature noticed for all the concentrations is that there is a strong change in the shear rate dependence of the viscosity $\eta$ at higher shear rates appearing to mimic a Newtonian plateau. The missing Newtonian plateau at low shear rates for the composites, except for the $X = 10$ is obvious and is reminiscent of the behaviour in highly filled fluids and the consequent immobilization of the network [41]. It should however be borne in mind that the defect network owing to the cholesteric structure of the medium may also be playing a role. In this context, the behaviour of the 10% composite is interesting. It exhibits a plateau at very low shear rates, followed by a sudden drop in $\eta$ values by nearly an order of magnitude. Subsequent variation (shear-thinning) is similar to the other composites and exhibits an additional plateau at high shear rates. Also it may be noticed that the $\eta$ value for this composite at the lowest shear rate is comparable to materials which form strong gels [42]. The strength of the gels with concentrations greater than 2% is also perhaps due to the cholesteric defect network being strongly aided by the H-bonded network of the GSC98 molecules. This effect could be so large for $X = 10$ that there is a breakdown of the network at $\dot{\gamma} \sim 2 \times 10^{-3} \text{s}^{-1}$. In fact, this concentration range is comparable to that in aerosil networks over which the nature of the gel changes over from weak to strong [39, 40]. A well-known expression for describing flow curves with a shear-thinning feature is the Carreau equation [43].

$$\eta(\dot{\gamma}) - \eta_\infty = (\eta_0 - \eta_\infty)(1 + (\lambda \dot{\gamma})^{2N})^{-N} \quad (2.2)$$

Here, $\eta_0$ and $\eta_\infty$ are the viscosity values at zero and very large values of the shear rate respectively, $\lambda$ indicates the rate of structural relaxation in the medium. It may be noted from figure 2.10 that $\eta_\infty$ is not well-defined and can be neglected. Thus equation 2.2 can be rewritten as follows:

$$\eta(\dot{\gamma}) = \eta_0 (1 + (\lambda \dot{\gamma})^{2N})^{-N} \quad (2.3)$$
The experimental data were fit to equation 2.3 by discarding the high shear rate part, which lies beyond the strong shear-thinning region. The exponent N, having values $0.35 \pm 0.02$ and $0.37 \pm 0.02$ for the two lower concentrations $X = 0.2$ and $0.4$, shows a marked increase for all other concentrations with the value lying in the range $0.6-0.66$. The fit also provides information about the relaxation rate $\lambda$, which is experimentally taken to be the inverse of the $\dot{\gamma}$ value at which there is a cross-over from the low-shear rate Newtonian plateau to the shear-thinning behaviour. Only for concentrations $X = 0.8$, 1, and 2, there is a clear tendency of a low-shear rate Newtonian plateau and the fitting is shown in the figure 2.11(a). Therefore, $\lambda$ can be unambiguously defined for these composites only, and the values obtained from the fit are $985 \pm 54$, $1669 \pm 70$, and $3863 \pm 751$ s, suggesting that the structural relaxation becomes slower with increasing concentration.

As mentioned above, a clear saturation in the viscosity value at low shear rates is not seen for most of the composites. Therefore, the value determined at a low shear rate of $1 \times 10^{-3}$ s$^{-1}$ is considered for observing the dependence of low shear rate viscosity $\eta_{\text{low}}$ on the gelator concentration $X$ and the result is shown in figure 2.11(b). A drastic increase in $\eta_{\text{low}}$ by more than 4 orders of magnitude when the concentration of GSC98 changes from 0.2

![Figure 2.11](image-url)
to 10% is observed. On a double-logarithmic scale, the variation is nearly linear with a slope of $2.4 \pm 0.2$, a value which is much lower than that, for example, seen in associating polymers which exhibit a transient network developed by entanglements [44].

### 2.3.6.2 Dynamic rheology measurements

Dynamic or oscillatory rheology measurements were performed to measure the complex modulus, $G^*(\omega) = G'(\omega) + G''(\omega)$ where $G'$ and $G''$ are the storage ($G'$) and loss ($G''$) moduli, of the composites. Two sets of measurements have been carried out. In the first set, the strain amplitude ($\gamma$) is chosen in such a way as to avoid the strain-driven structural deformation and the rheological response is studied as a function of angular frequency ($\omega$). In the second set of measurements, $\omega$ is fixed and $\gamma$ is varied to determine the response of the sample through the linear and the non-linear regime.

(a) **Linear viscoelasticity**

The variation of $G'$ and $G''$ with $\omega$ obtained at a constant strain amplitude (in the linear response regime) is shown in figure 2.12 (a,b) for six concentrations, with $X=0.2$ to 10. The composites with $X < 4$ exhibit, at low frequencies, a frequency-independent plateau.

![Figure 2.12](image-url)

**Figure 2.12:** Angular frequency ($\omega$) dependence of the two moduli $G'$ and $G''$ obtained with small strain amplitude. The low concentrations exhibit, above a certain value of $\omega$, a frequency-dependent $G'$, which can be described by slope values between 1 and 2 (indicated by slope lines 1 and 2). The higher concentrations are essentially frequency independent over the entire range of $\omega$. 
suggesting that the material contains cooperative rearrangements as in rubber polymers [45].
For these composites above a concentration dependent frequency, a scaling regime is seen for
both the moduli; noticeable is the fact that $G'$ remains greater than $G''$ until the highest
frequency of measurement, although there is a trend that at much higher values there may be
a cross-over. For $X \geq 4$, the plateau region extends over the entire range of frequencies. These
features are qualitatively similar to that of lightly cross-linked polymer bundle systems [46].
To check if the behaviour is similar on a quantitative level as well, the data in the scaling
regime were fit to a power law of following form:

$$G' \sim \omega^z$$

The fitted $z$ value turned out to be in the range 1.0-1.7, which is much higher than 0.75,
expected for the cross-linked polymers [47] indicating that the comparison is only qualitative.
An additional feature to be noted is that even at the lowest frequency the liquid-like
behaviour ($G'' > G'$) is not seen, pointing to the fact that the structural relaxation times are
very large, characteristic of gels. As mentioned earlier, in the case of SGMs, over the low and
medium frequency regime, the SGR model proposes a power-law dependence for $G'$ and $G''$.
Recalling equation 2.1, the power law dependence of the moduli on $\omega$ is expressed as
follows:

$$G' \sim \omega^{x-1} \text{ and } G'' \sim \omega^{x-1}$$

The model expects the noise temperature $x$, to be the same for both the moduli and the
exponent $(x-1)$ to be of small magnitude. The data are fit to equation 2.1 in the low frequency
region. The $G''$ data having a slightly higher noise level in the low frequency regime lead to
larger error bars when such a power-law fitting is performed. For $X = 0.2$, the influence of the
noise level is high enough to prevent the fitting being performed with any level of
confidence. It may be remarked here that but for $X = 0.8$, the rest of the composites have a
negative slope for $G''$ ($G''$ decreases with increasing $\omega$) in the range of 0.1-1 rad/s. In all the
Figure 2.13: Dependence of $G''$ on $\omega$ in the low angular frequency region for different concentrations ($X$), exhibiting a shallow minimum. The data in the $\omega$ range $10^{-1}$ to 1 rad/s are fit to equation 2.1, represented by solid lines.

In some cases, the data in this range were used for fitting $G'$ and $G''$ data to equation 2.1. The quality of fitting can be judged from the data presented on an enlarged scale for $X=2$, 4, 6 and 10 in figure 2.13. A shallow minimum is seen in the $G''$ data at low frequencies and such a range-limiting fitting procedure as shown in the figure has been used in literature [48] to determine the exponent. The exponent ($x-1$) values obtained by fitting the $G'$, $G''$ vs. $\omega$ data are shown in figure 2.14. The fact that the values are quite low is in good agreement with the predictions of the SGR model, although the exponents for the storage and the loss moduli data are slightly different from each other. It may be pointed out that with increasing concentration while the exponent for the $G'$ data does not show any systematic variation, the exponent for the $G''$ data appears to decrease. The low value of the exponent is expected for physical
networks, indicating that the strands of the H-bond dictated network dynamically break and form, a feature universal for a wide variety of soft materials such as slurries, paints, microgels, foams, etc. The SGR model also expects that the exponent \((x-1)\) is given by the ratio \(G''/G'\). The ratio turns out to be 0.08 to 0.13 for the different concentrations. These values are definitely higher than the values of \((x-1)\). The exact reason for this discrepancy is still unknown. Notwithstanding the fact that in the present system there is an additional defect network, caused by the cholesteric structure, the very presence of the anisotropic liquid crystal itself may also introduce the difference.

To investigate the role played by the cholesteric defect network, the frequency dependence of the moduli were determined by pre-shearing the sample for 10 min at a shear rate of 5 s\(^{-1}\) for \(X < 2\) composites and 500 s\(^{-1}\) for gels \(X \geq 2\). It is well-known that such a treatment results in the alignment of the cholesteric structure and therefore these results can be considered to be due to the defect network that gets formed even in pure cholesteric materials without any gelating substance. (It should be noted here that the host material E7 is achiral, and therefore the peptide molecule plays a dual role of imparting chirality as well as

Figure 2.14: Concentration \((X)\) dependence of (a) the exponent \((x -1)\) obtained from a power-law fitting of the data (represented as solid lines in figure 2.13) in the low frequency regime.
initiating gelation in E7). Figure 2.15(a) shows the frequency dependence of the $G'$ before and after the pre-shear treatment for three representative concentrations $X = 0.4, 2, \text{ and } 4$, and it is seen that $G'$ decreases on the application of the pre-shear. In other words, the applied pre-shear diminishes the defects in the network bringing down the modulus [49]. For $X = 10$ gel, owing to its large strength, the applied pre-shear may be insufficient to cause this before any irreversible rupture takes place.

The strength of the gels can be characterized by the magnitude of the plateau modulus $G'_{\text{plateau}}$, taken as the $G'$ value at the lowest frequency ($\omega = 0.1 \text{ rad/s}$). A plot of $G'_{\text{plateau}}$ as a function of gelator concentration is shown in figure 2.15(b): $G'_{\text{plateau}}$ increases with $X$ and the dependence is described by a scaling law, $G'_{\text{plateau}} \sim X^{2.43 \pm 0.02}$.

(b) **Non-linear Viscoelasticity**

To establish the limits of the linear viscoelastic regimes, the strain amplitude ($\gamma$) dependence of $G'$ and $G''$ moduli were determined. The results are shown for a representative concentration $X = 0.8$ in figure 2.16. It may be mentioned here that most colloidal suspensions...
and polymer solutions show a simple yielding behaviour, where both $G'$ and $G''$ decrease monotonically as $\gamma$ increases \[50\]. In contrast, the strain-amplitude behaviour of the gels studied here can be divided into two regimes. Figure 2.16 shows that at low amplitudes, $G'$ is nearly constant, suggesting a linear viscoelastic regime (LVR). Here $G'$ is higher than $G''$, exhibiting the solid-like behaviour of the gel. Above a critical strain amplitude ($\gamma_c$), determined by drawing tangents to the data in the low and high strain ranges, and found to be 0.03 for $X=0.8$ (indicated by an arrow in figure 2.16), both moduli become strain dependent with $G'$ decreasing and $G''$ passing through a maximum before decreasing as well. As the strain amplitude increases further (beyond $\gamma_c$), $G'' > G'$ and the sample becomes more liquid-like. This signals a deformation-driven transition from a viscoelastic solid to a viscoelastic liquid.

The observation of a peak in $G''$ and a monotonic decrease in $G'$ are hallmarks of soft glassy materials \[51, 52, 53\] and is expected theoretically below the 'noise temperature' $\theta$. The data are analysed using the following two empirical expressions:

![Figure 2.16: Elastic moduli (filled circles, $G'$; open circles, $G''$) data, shown for a representative concentration $X = 0.8$, can be quite well described over the entire range of $\gamma$ using equations 2.5 and 2.6 depicted as lines.](image-url)
Equation 2.6 is the more generalized version of the one used by Colby et al. [54], by the introduction of the exponent \( m \). In fact, forcing \( m = 1 \) (as in Colby’s) will make the fit decay slower than the data. To retain the general feature of above equation and also to account for the peak in the \( G'' \) data, an additional term is introduced in the numerator, the form of which is influenced by empirical equations, such as Cole-Davidson, employed to describe the dielectric dispersion data. The additional exponent \( n \neq m \) is necessitated by the observation that the \( G'' \) profile is asymmetric about the peak point. The solid lines in figure 2.16 show that the equations 2.5 and 2.6 fit the data quite well (with \( m = 0.58 \pm 0.06, n = 1.28 \pm 0.03 \)), supporting the soft glass rheological character of the E7-GSC98 gels.

Above the critical strain, the decay in the storage and loss moduli are described by the following expressions:

\[
G' \sim y^v' \quad \text{and} \quad G'' \sim y^v''
\]

with \( v' = 1.31 \pm 0.01 \) and \( v'' = 0.64 \pm 0.01 \), i.e., \( v'' \sim v'/2 \), as observed for SGMs [55].

Studying the general behaviour of complex fluids subject to large amplitude oscillatory strain (LAOS), Hyun et al. [56] have classified the trends observed beyond \( \gamma_c \) into four categories: (i) Type I, strain softening (both \( G' \) and \( G'' \) decrease monotonically), (ii) Type II, strain hardening (both \( G' \) and \( G'' \) increase monotonically), (iii) Type III, weak strain overshoot (\( G' \) decreasing monotonically, \( G'' \) exhibiting a peak) and (iv) Type IV, strong strain overshoot (both \( G' \) and \( G'' \) exhibiting peaks). The LAOS behaviour for different concentrations is shown in figure 2.17. For convenience of presentation, the data sets have been normalized by taking the ratio \( G'/G'_o \) (upper panel) and \( G''/G''_o \) (lower panel), where \( G'_o \)
and $G''_0$ are the plateau in $G'$ and maximum in $G''$ values, respectively. It is seen that all the concentrations, except $X = 0.2$, display the type III or weak strain overshoot behaviour,

![Graph showing strain amplitude dependence of the normalized storage (upper panel) and loss (lower panel) moduli for composites with X=0.2, 0.8, 2, and 6. Below a certain critical strain $\gamma_c$, $G'$ is independent of $\gamma$ but exhibits a strong decrease above it. $G''$ shows a similar signature only for $X = 0.2$ but has a peak for all other values of $X$, corresponding to type I and type III behaviours respectively, discussed in the text. The higher concentration composites exhibit a weak strain hardening ($G'$ increasing as $\gamma$ increases from a low value) just before $\gamma_c$, as in the example shown in the inset (a) for $X = 6$. The $G'$ vs $\gamma$ data in the non-linear regime (i.e., above $\gamma_c$) have been fit to a straight line (in the log-log scale), the slope of which is shown as a function of $X$ in inset (b). Inset (b) also shows that the critical strain $\gamma_c$ decreases with $X$, in a power-law fashion.]

Figure 2.17: Strain amplitude dependence of the normalized storage (upper panel) and loss (lower panel) moduli for composites with $X=0.2, 0.8, 2, 6$. Below a certain critical strain $\gamma_c$, $G'$ is independent of $\gamma$ but exhibits a strong decrease above it. $G''$ shows a similar signature only for $X = 0.2$ but has a peak for all other values of $X$, corresponding to type I and type III behaviours respectively, discussed in the text. The higher concentration composites exhibit a weak strain hardening ($G'$ increasing as $\gamma$ increases from a low value) just before $\gamma_c$, as in the example shown in the inset (a) for $X = 6$. The $G'$ vs $\gamma$ data in the non-linear regime (i.e., above $\gamma_c$) have been fit to a straight line (in the log-log scale), the slope of which is shown as a function of $X$ in inset (b). Inset (b) also shows that the critical strain $\gamma_c$ decreases with $X$, in a power-law fashion.
whereas the type I feature is seen for $X = 0.2$. In fact, a gentle strain hardening can be seen, especially for $X = 4$ and 6 composites (shown for $X=6$ in the inset of figure 2.17, upper panel), at strain values lower than $\gamma_c$. For $X = 6$, value of $G'$ increases by about 30% when the strain value is increased from $10^{-4}$ to $\gamma_c$. The enhancement in $G'$ appears to be maximum for $X = 4$ and decreases for higher as well as lower concentrations. In the non-linear region ($\gamma > \gamma_c$), the data can be fit to a straight line (in the log-log scale). The slope of such a line (indicated by open circles) is plotted as a function of concentration in inset (b) of figure 2.17 (upper panel); the data show that the higher concentration composites have a similar non-linear rheological behaviour. The concentration dependence of this slope can, in fact, be described by a power-law, with an exponent of 0.2. The critical strain (filled circles, inset (b)) on the other hand decreases with concentration. Such behaviour is expected for gels, where the gel strength increases with increase in gelator concentration [42]. The $\gamma_c$ vs. $X$ data can also be expressed as power-law function with an exponent of 0.86.

(c) Complex Viscosity

Recalling from chapter 1, the complex viscosity can be determined from dynamic rheological measurements using the following expression:

$$\eta^* = \frac{\sqrt{G'^2 + G''^2}}{\omega}$$ (2.8)

In Maxwellian fluids, as per the Cox-Merz rule, $\eta$, the viscosity determined from steady state measurements, and $\eta^*$, determined from equation 2.8, are identical. This superposition is not applicable for weak gels as well as soft glassy systems, a feature that is predicted by SGR model [22]. Further, the frequency dependence of $\eta^*$ can be described by a power-law of the following form:

$$\eta^* \sim \omega^{-p}$$ (2.9)
Figure 2.18: Frequency dependence of the complex viscosity $\eta^*$ determined from oscillatory measurements (open symbols) using equation 2.8 and shear viscosity from steady state measurements $\eta$ (filled symbols). The lines represent fit to equation 2.9. The exponent obtained, being nearly equal to a value of 1, suggests solid-like response of the system seen in well-formed gels. The fact that $\eta^*$ and $\eta$ do not coincide indicates the breakdown of the Cox-Merz superposition.

Here, values of $p$ close to zero suggest liquid-like behaviour and, if close to 1, a solid-like response [57].

Figure 2.18 clearly shows the failure of the Cox-Merz superposition for two representative concentrations, $X = 0.8$ and 10. To fit to equation 2.9, the $\eta^*$ data over the entire frequency span were considered for $X=10$, whereas for $X=0.8$ it was limited up to $\omega=10$ rad/s, owing to a slope change above that frequency. It can be seen that equation 2.9 describes the data well in both cases and the $p$ values so obtained, $0.966 \pm 0.003$ and $0.952 \pm 0.001$ for $X = 0.8$ and 10 respectively, establish the solid-like response of the system, a feature seen in well-formed gels [57].

2.3.6.3. Gel collapse and recovery

Transient measurements show that the NLC-GSC98 gels can collapse and, more importantly, recover its rheological properties on very fast time scales. For these studies, the gel materials were subject to large amplitude oscillations with the strain values in the non-linear regime ($\gamma > \gamma_c$) resulting in the breakdown of the gel structure. Subsequently, the strain amplitude
Figure 2.19: Step strain measurements with \( \omega = 1 \) rad/s for \( X = 2 \) gel showing the rapid recovery of gel structure when the gel is subjected to a large oscillatory strain of 0.4 (regions indicated as High). The initial low strain amplitude is \( 3 \times 10^{-3} \) (regions marked Low). The recovery to the gel state takes place within ~20 s and is reproducible over repeated cycles of measurement.

was abruptly reduced to a very small value (\( \gamma < \gamma_c \), to be in the LVR region) while monitoring \( G' \) and \( G'' \). The results for a representative concentration \( X=2 \) performed by applying consecutive cycles of oscillatory strain is shown in figure 2.19; the parameters during this experiment are \( \omega=1 \) rad/s, low \( \gamma=3 \times 10^{-3} \) and high \( \gamma =0.4 \). As expected, at large strain values, \( G' \) decreases by orders of magnitude and also becomes smaller than \( G'' \). When \( \gamma \) is reduced to a small value, the recovery to the elastic state starts instantaneously, requiring less than 20 s. The recovery is indeed reproducible over repeated cycles of measurement. A point to be noted is that the recovery to the original values is nearly complete over very short time scales for the low concentration composites (\( X<6 \)).

However, for higher concentrations (\( X\geq6 \)), although the return to the elastic state is initiated when the strain value was reduced, there appeared to be two stages in the complete recovery. This is shown on an enlarged scale in figure 2.20 for three concentrations \( X= 0.2, 0.8 \) and 6. For \( X = 0.2 \) and 0.8, most of the recovery takes place almost instantaneously upon removal of the large strain. In contrast for the \( X = 6 \) two time scales with a partial instant
Figure 2.20: Gel recovery after removal of the High γ. While for the low concentrations (X = 0.2 and 0.8) most of the recovery takes place almost instantaneously upon removal of the large strain, for the X = 6 there appears to be two time scales with a partial instant recovery of normalized modulus and a slow increase (until about 200s⁻¹) toward an overall background variation that appears to be common for all X beyond about 300 s.

recovery and a slow increase (until about 200s⁻¹) toward an overall background variation are seen, a feature common to all X beyond 6.

2.4. Conclusion

In this chapter, results of calorimetric and extensive rheological measurements that have been carried out on a NLC host gelated using a novel dipeptide based organogelator, also a liquid crystal, are described. Being a chiral material, the gelator induces helical structure to the gel fibres and also imparts chirality to the nematic phase of the otherwise non-chiral LC. DSC studies indicate features similar to that of the random dilution to random cross-over behaviour seen in aerosil-LC gels. Apart from displaying the standard features of gels, the rheological measurements bring out the soft glassy characters of the composites. These materials also show a fast recovery to the gel state after the removal of a large strain. The elastic and viscosity parameters appear to be influenced by the defect network of the
cholesteric liquid crystalline state as well as the network formed due to the H-bonding amongst the peptide molecules.

2.5. References


