Electro-rheological effect of blends composed of two liquid crystalline materials: composition dependence

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The electro-rheological (ER) effect of blends composed of two liquid crystalline materials (polymer and oligomer) with varying volumes of each component is discussed in this article. The results indicated that the ER effect of each blend was observed at a different temperature range. The blends showed better ER response to an applied electric field compared with each neat sample. Also investigated is the behaviour of the liquid crystalline oligomer in the isotropic polymer under an applied electric field, by polarising optical microscope observation. This study demonstrates the importance of a host matrix in blend systems on ER effect.

Keywords: electro-rheological effect; blend; liquid crystal; siloxane; rheology

1. Introduction

Liquid crystals have attracted much attention in the field of engineering. Their application to the development of screens and displays is a good example, as liquid crystals have the useful quality of molecular orientation. In order to develop further the utility of liquid crystals, we have investigated the electro-rheological (ER) effect, in which viscosity is controlled by the strength of an applied electrical field. ER fluids have been widely studied as smart materials for industrial utilities since the ER effect was first discovered by Winslow in 1949 [1]. ER fluids are divided into two types, on the basis of the component of the fluids and the mechanism of appearance of the effect. One is called the heterogeneous type, in which dielectric particles are dispersed in an insulating oil such as silicone oil. The ER effect in this system is caused by formation of clusters and chains built up by polarised dielectric particles between electrodes under an applied electric field. The other is called the homogeneous type, which consists of single fluid such as liquid crystalline materials. The assumed mechanism of the latter case is that anisotropic domains made by oriented moieties within the molecules generate resistance to shear flow, resulting in changes in shear stress [2].

In our laboratory, we have studied the ER effect of liquid crystalline materials such as side chain liquid crystalline polymers composed of siloxane backbones, and liquid crystalline oligomers composed of cyclic siloxane chains [3–6]. However, the liquid crystalline polymer did not show a useful ER effect because of its high inherent viscosity, which obstructed the orientation of the mesogens, leading to a slow response. On the other hand, the oligomer showed small changes in shear stress with a good response time only in a low shear rate range. In addition, a large shear strain induced a slip between smectic layers comprising the oligomer, resulting in a decrease of shear stress.

Our next approach shifted to the investigation of the ER effect in a blend system using these liquid crystalline materials. In conventional techniques, dilution of polymers with high viscosity by an insulating oil such as silicone oil has been carried out [7]. Therefore, the dilution was performed with the aim of improving the ER effect of the polymers.

In the present work, the ER effect in the blend system is investigated on the basis of the concept that the isotropic polymer matrix covering the liquid crystalline oligomer plays a key role in preventing the slipping behaviour that occurs in the smectic phase, which disturbs the positive ER effect. The slipping of the oligomer might be avoided with the existence of the polymer in the isotropic state. It would become fairly easy to form the smectic domains of the oligomer.

The results indicated a remarkable ER effect, with quick response to the applied electric field at the temperature range, where each neat sample did not show any ER effect. Here we show the ER effect of blends composed of the liquid crystalline polymer and the liquid crystalline oligomer, and the volume fraction of each component in the blend is changed in order to study the variation in ER response as a function of the given shear rate and the field strength. Also demonstrated is how the liquid crystalline oligomer in the blend behaves under an applied electric field, through polarising optical microscope (POM) observation.

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2.   Experimental details

2.1   Samples

Structures of the polymer and the oligomer are shown in Figure 1. Both the polymer and the oligomer were prepared by a typical hydrosilylation according to the literature [3–6]. Their phase transition behaviour, obtained from differential scanning calorimetry (DSC) and POM, is summarised in Table 1. The two samples were mixed in a ratio of 1:4, 2:3, 3:2, 4:1 (polymer:oligomer) by weight. Prior to all measurements done in this study, the blend was kept in full isotropic state at 120°C for 10 min.

2.2   Characterisation

Thermal properties were measured with Diamond DSC (PERKIN ELMER) with heating and cooling rates of 5°C min^{-1}. The textures of the liquid crystalline phases were observed with a Nikon ECLIPSE E600 polarising optical microscope equipped with a METTLER TOLEDO FP-82HT hot stage and a METTLER TOLEDO FP-90 central processor.

2.3   Rheological measurements

The rheological properties were measured by a rotational rheometer (Rheosol-G2000, UBM Ltd.) equipped with an electric field controller (Matsusada Precision Devices high-voltage supply). All measurements were performed using parallel plates with a diameter of 15 mm and a gap of 0.1 mm. First, the sample mounted between the parallel plates was heated to a temperature in the isotropic state, and maintained for 10 min. Then, it was cooled step by step to the measuring temperature, or well inside the smectic A phase, respectively. After each cooling step, the sample was kept at the measuring temperature for at least 45 min to ensure an equilibrium state before the measurements were started. An electric field of 2, 4, or 6 kV mm^{-1} was applied between upper and lower plates under steady shear flow at a constant shear rate (50 s^{-1}). Generated shear stress was defined as the

Table 1. Phase transition behaviour of the polymer and the oligomer on cooling (5°C min^{-1}).

Sample		Tg / °C		Tcl / °C	
Polymer	G	−8	SmA	48	I.L.
Oligomer	G	−11	SmA	109	I.L.

Note: G: glass state, SmA: smectic A, I.L.: isotropic liquid

difference between the measured shear stress in the presence and absence of the application of the electric field. Shear rates reported in this paper have been defined as the shear rate at the edge of the plate, because the fixtures did not provide a uniform shear strain.

3.   Results and discussion

3.1   Phase transition behaviour

The phase transition behaviour of the liquid crystalline materials was characterised by POM and DSC [4, 6]. The oligomer showed bâtonnet texture at the clearing point on cooling from the isotropic melt. The texture then changed gradually with decreasing temperature; consequently a focal conic fan texture was formed. The polymer also showed focal conic fan texture in the liquid crystalline phase after annealing.

For each blend, the appearance of bâtonnet texture was observed in the cooling process from the isotropic liquid phase. The temperature at which the bâtonnet texture appeared was in agreement with the clearing point of the liquid crystalline oligomer (109°C). When passing though the clearing point of the liquid crystalline polymer (48°C), the retained dark area under POM was filled with an anisotropic domain by formation of the liquid crystalline phase. From these observations, the two components in the blend formed their liquid crystalline phase independently. This indicated that they were immiscible with each other and micro phase separation occurred in the blend.
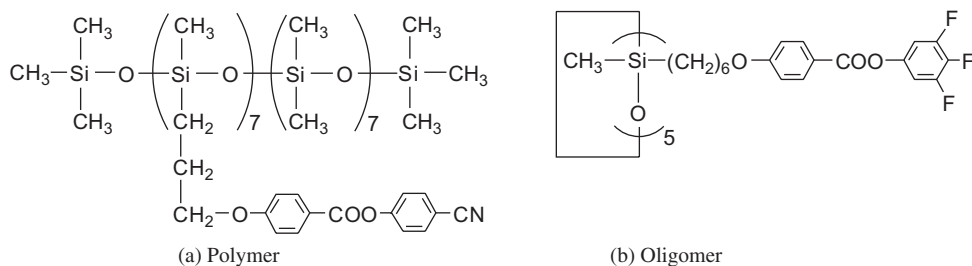

Figure 1.   Structure of neat liquid crystalline materials; (a) side chain liquid crystalline polymer, (b) cyclic-siloxane oligomer.

3.2   Rheological properties

3.2.1   ER effect of the blend

In this section, ER effect for a blend (polymer:oligomer = 3:2) at each temperature is discussed as an example. Temperature dependence on the ER effect for the blend is shown in Figure 2(a)–2(d). An electric field of 2, 4, and 6 kV mm^{-1} was applied to the blend for 100 s under a constant shear rate of 50 s^{-1}. As seen in these figures, the ER effect obtained was drastically influenced by the given temperature. The ER effect became recognisable from 90°C. The generated shear stress at each magnitude of electric field apparently increased with decreasing temperature. In the temperature range from 90°C to 60°C, the shear stress increased sharply after applying the electric field and reached a maximum value. The shear stress then recovered immediately upon removal of the electric field. A relatively large ER effect was observed at 70°C, resulting in variation of shear stress from 1050 Pa under no electric field to 1450 Pa under an electric field of 6 kV mm^{-1}.

In contrast to the ER effect of polymers with high viscosity [7–10], a fast response in shear stress was realised with the following changes in the electric field. Upon applying an electric field of 6 kV mm^{-1}, the measured shear stress rose rapidly to a much larger value within a short period of time, in the order of a few seconds. The shear stress immediately approached a steady value which was larger than the corresponding value in the absence of the electric field. The ultimate steady state was stable to a prolonged shearing. Upon removal of the electric field, the shear stress rapidly returned to the value measured before applying the electric field. As a comparison, the stress response to an electric field of 2 and 4 kV mm^{-1} at
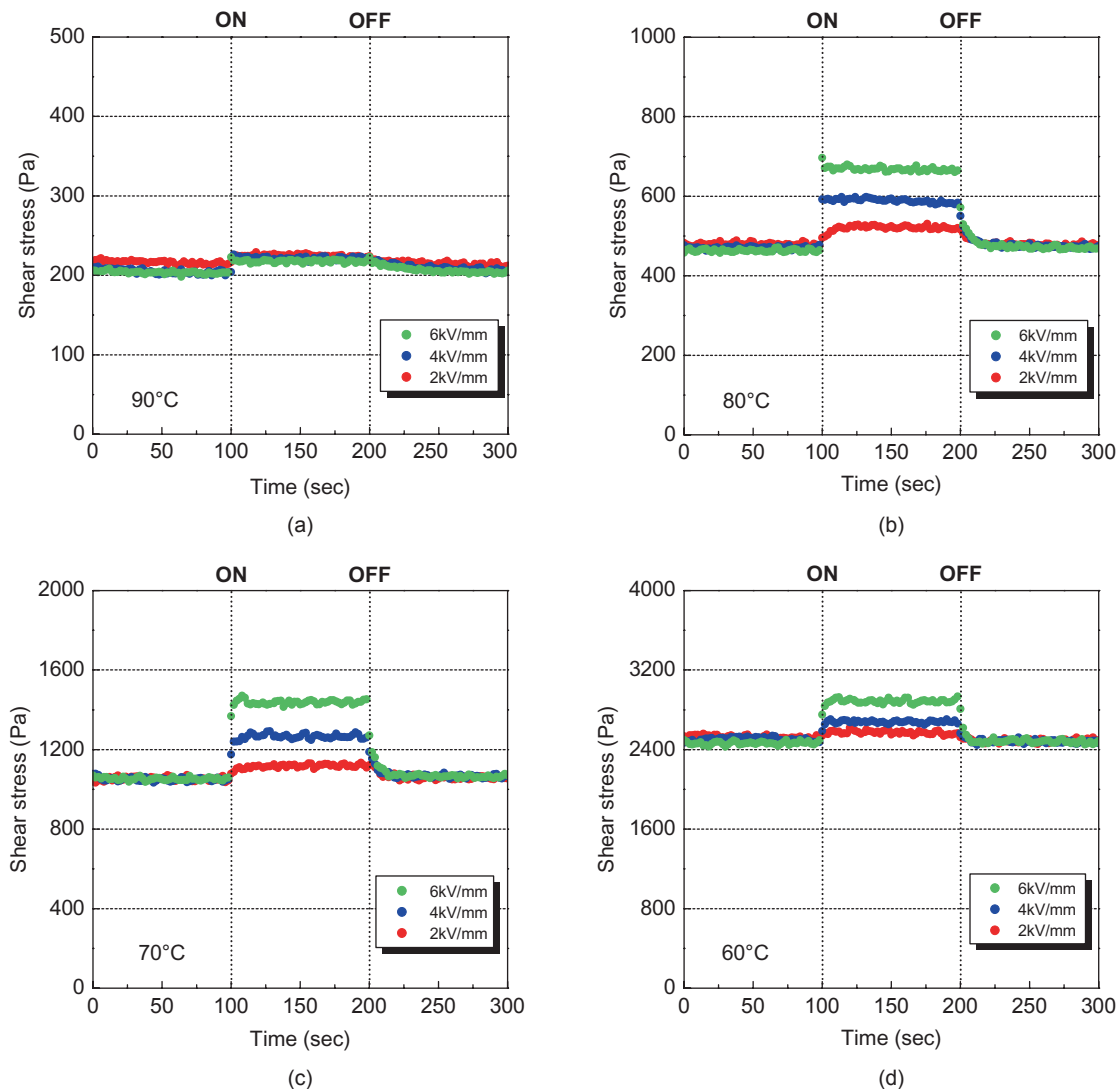

Figure 2.   Temperature dependence on the ER effect for the blend: (a) 90°C, (b) 80°C, (c) 70°C and (d) 60°C (colour version online).

the shear rate of 50 s^{-1} is also shown in Figure 2(a)–2(d). Clearly, the increase in the shear stress was observed under each field. The dispersed domains consisting of the liquid crystalline oligomer could elongate and form bridge structures in the liquid crystalline polymer in the isotropic phase between electrodes [11]. Below 60°C, an effective ER effect could not be obtained because of the unstable shear stress in the absence of the electric field.

3.2.2   Generated shear stress of each blend as a function of temperature

The generated shear stress at a constant shear rate (50 s^{-1}) for various blends is shown in Figure 3. A field strength of 6 kV mm^{-1} was applied to the blends. It was found that no ER effect was observed over 110°C in the isotropic state for both the polymer and the oligomer. The temperature range in which the ER effect was obtained differed depending on the content of each blend. The blend which contained more oligomer than polymer showed the ER effect in a higher temperature range. For the blend (polymer:oligomer = 1:4), the appearance of the ER effect was observed in a narrow range from 90°C to 100°C. This range is just below the clearing point of the oligomer.

This trend in the appearance of the ER effect was similar for other blends. The generated shear stress increased gradually with decreasing temperature for each blend. The maximum value in the generated shear stress was approximately 400 Pa. These blends showed an increase in shear stress in the absence of an electric field with decreasing temperature. This is caused by a reduction in the molecular motion of the polymer towards its clearing point (48°C). Therefore, the
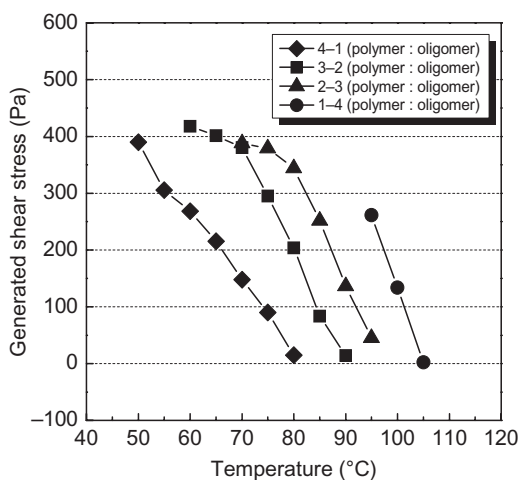
smectic domains consisting of both the polymer and the oligomer are wholly formed in the blend below 50°C, so that the high viscosity prevented the appearance of the ER effect.

According to the fundamental concept of the appearance of the ER effect in the blend system, it is assumed that the smectic domains consisting of the oligomer could elongate and form bridge structures in the polymer in the isotropic phase between electrodes [11]. In previous work [4], we observed a decrease in shear stress in the presence of the electric field for the neat oligomer. This behaviour was caused by the slippage between the smectic layers. However, in the case of the blends, the polymer in the isotropic phase covers the oligomer, and its viscosity controls the slip.

3.2.3   Shear rate dependence on ER effect for the blend

Figure 4 shows shear stress at various shear rates for the blend (polymer:oligomer = 2:3) at 65°C. Changes in the shear stress upon application of the electric field are particularly pronounced in a given shear rate range. Higher strengths of applied electric field resulted in a considerable increase in shear stress. Generated shear stress of 2000 Pa was obtained at 350 s^{-1} under 6 kV mm^{-1}. Other samples also showed a similar behaviour.

As we reported previously, a gradual decrease in shear stress under applied electric field for the neat oligomer in the smectic phase was observed [4]. This behaviour may be caused by the slippage between smectic layers under shear flow. In addition, low molecular weight liquid crystalline materials tend to flow by shear strain with high shear rate. This results in no increase in shear stress, even if molecular orientation

Figure 3.   Generated shear stress at a constant shear rate (50 s^{-1}) for each blend.
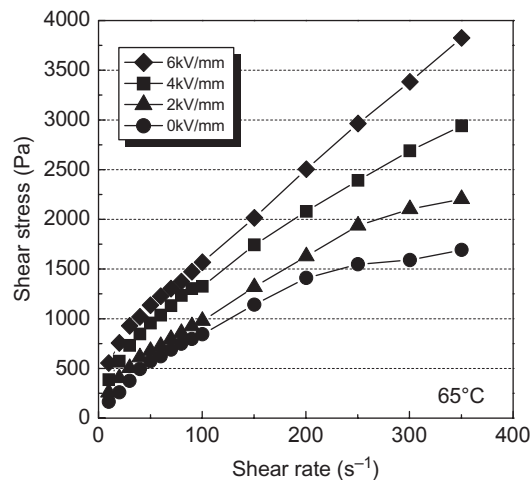

Figure 4.   Shear rate dependence on ER effect for the blend (polymer:oligomer = 2:3).

occurs under an applied electric field. This behaviour is the main disadvantage in the use of ER fluids, though response speed to applied electric field is very fast. In the blends in this study, the polymer matrix with higher viscosity covers the oligomer and prevents the oligomer from flowing. As a result, a large increase in shear stress was obtained in a high shear rate range.

3.2.4   *Response time as a function of temperature*

Response to the application of an electric field as a function of temperature is described in this section. Shear stress of the blend (polymer:oligomer = 2:3) at 55°C, 65°C and 90°C is shown in Figure 5. As mentioned previously, the change in shear stress by the application of an electric field is greatly affected by temperature. At 90°C, ideal behaviour of the ER effect was obtained though decrease of change in shear stress was avoidable in the high temperature range. After the application of the electric field, the shear stress sharply reached a maximum value. Recovery of the shear stress at 200 s was also very fast. The shear stress in both the presence and the absence of the application of an electric field was extremely stable. Also at 65°C, excellence in response to the application of the electric field was observed. Compared with that at 90°C, the inherent shear stress increased and a generated shear stress of 350 Pa was obtained. The behaviour at 55°C differed from that in higher temperature ranges. The shear stress increased to 1600 Pa, and its irregularity was additionally observed in the absence of the application of an electric field. The shear stress responded quickly to the applied electric field at 100 s. However, it resulted in a delay to its maximum shear stress. In addition, a gradual decrease in shear stress after the

removal of the electric field was observed, with approximately 50 s necessary to attain its former viscosity.

Even if a large difference in shear stress by the application of an electric field can be obtained, a poor response is a disadvantage for engineering purposes. As shown in Figure 5, the shear stress in the absence of the electric field increased in the lower temperature range, which was mainly due to the polymer matrix. This prevents the oligomer from making enhanced domains in the polymer matrix with higher viscosity. This resulted in a delay of change in shear stress.

3.3   *POM observation under an applied electric field*

The optical investigations of the blend (polymer:oligomer = 1:4) under an applied electric field were carried out in a transparent sandwich-type cell consisting of two glass plates coated with indium tin oxide (ITO). For the blend of the ratio 1:4 (polymer:oligomer), homeotropic alignment of the smectic domains consisting of the oligomer can be successfully achieved between ITO substrates by AC electric fields.

As mentioned before, the polymer and the oligomer in the blend formed their liquid crystalline phases independently. Below the clearing point of the oligomer (109°C), the smectic domains consisting of the oligomer were observed in the cooling process from the isotropic liquid. The POM image in the absence of an applied electric field at 90°C is shown in Figure 6(a). The dark area in the image was due to the isotropic polymer. When an AC electric field (2 V μm^{-1}, 1 kHz) was applied to the ITO cell, the POM image became optically isotropic within a few seconds, though complete darkness was not achieved, as shown in Figure 6(b). This result clearly indicates that the smectic domains are aligned perpendicular to the surfaces of ITO electrodes. Better alignment was achieved in proportion to the magnitude of the applied electric field, as shown in Figure 6(c) and 6(d). There was no difference in response speed of the homeotropic alignment over the range of 2 V μm^{-1} to 6 V μm^{-1}. After removing the electric field, the textures appeared again within a few seconds, which means that the domains naturally reverted to a random orientation.

This alignment behaviour surely corresponds to the result of rheological measurement under the applied electric field. These observations suggest that the homeotropic alignment of the oligomer in the isotropic polymer plays a key role in the increase in viscosity. Another important point is that the isotropic polymer covers the smectic domains and facilitates the formation of the domains along the electric field. As reported previously, the smectic domains
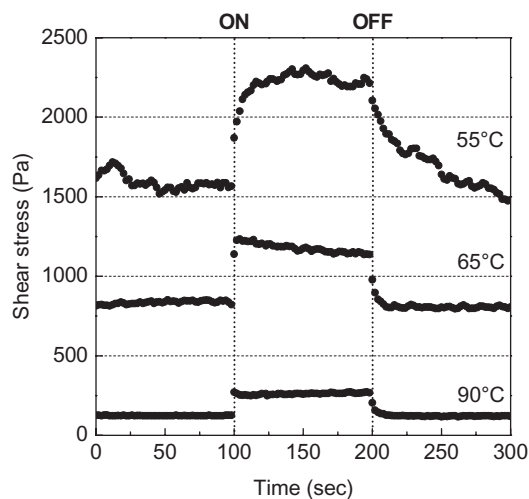

Figure 5.   Shear stress of the blend (polymer:oligomer = 2:3) under 6 kV mm^{-1} at 55°C, 65°C and 90°C.
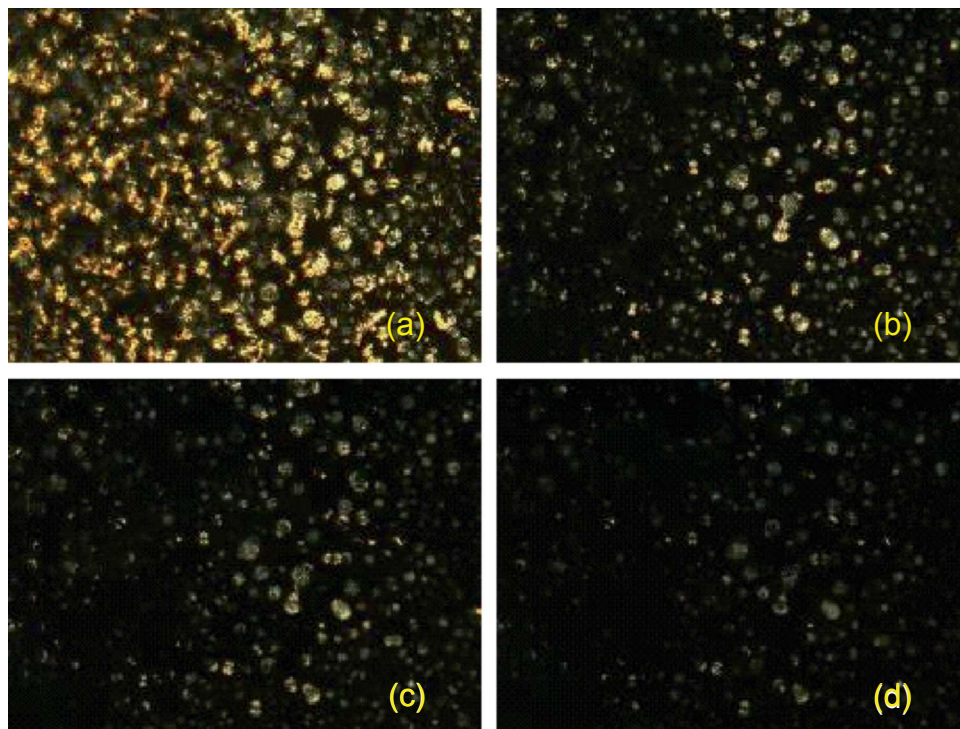
Figure 6.   Polarising optical microscopy images at 90°C under an electric field (1 kHz): (a) 0 V μm^{-1}, (b) 2 V μm^{-1}, (c) 4 V μm^{-1} and (d) 6 V μm^{-1} (colour version online).

without the polymer caused slippage between the smectic layers under the applied electric field and did not show an increase in viscosity [6]. After the removal of the application of the electric field, the enhanced shear stress is consequently restored to its former state immediately, because there is no driving force to make the oriented domains that act as the resistance to the shear flow.

4.   Conclusions

We have presented the observation of an ER response in the blend system. The response characteristics under different conditions were examined. ER responses in the blends with different volume fractions of each component have been investigated over a wide range of shear rate following the application of electric fields of 2, 4, and 6 kV mm^{-1}.

A better response to the application of the electric field, and a bigger increase in shear stress, was observed in the blends compared with the ER effect in each individual component. In addition, a stable value in shear stress under the electric field was obtained in the blend system, while the neat oligomer showed a transient decrease in shear stress because of the slips between smectic layers.

This research is aimed at improvement in the ER effect of the oligomer which is greatly influenced by shear strain, which leads to the slipping. The oligomer in the isotropic polymer could be oriented as usual under the applied electric field. Furthermore, the molecular orientation of the oligomer was not hindered by the isotropic polymer, which is far from its clearing point. The ER effect in this system could be improved by tuning a composition and a suitable balance of viscosity. In this sense, the combination of the smectic domains and the isotropic polymer led to an enhanced ER effect.

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