Polymer Journal, Vol. 26, No. 12, pp 1402—1404 (1994)

SHORT COMMUNICATIONS

Induced Network Structure in Liquid Crystalline Polymer Evidenced from Electrorheological Normal Stress Measurements

Hiroshi KIMURA, Keiji MINAGAWA, and Kiyohito KOYAMA†

Department of Materials Science and Engineering, Yamagata University, Jonan, Yonezawa 992, Japan

(Received August 5, 1994)

KEY WORDS Electrorheology / ER effect / Homogeneous ER fluid / Liquid Crystalline Polymer / Normal Stress / Polarizing Microscopy /

Electrorheological (ER) fluids are defined as the materials to display reversible changes in rheological properties under applied/removed electric field. The ER fluids have received increased attention because of the possibility of many applications and the academic point of view. The overview of the ER fluids can be found in the reviews.[1-3] Many ER studies have concentrated on the suspensions from the Winslow's report.[4] The understanding of the Bingham stress response and the chain formation of the suspended particles, which are main aspects of the ER suspensions, have been developed recently. However, the sedimentation of particles is a problem for ER suspensions. Thus sedimentation free ER fluids have been demanded from the application view point. The ER effects of some homogeneous liquids without particles have been attempted.[5-8] Among them, polymers with flexible side chain connected with polar mesogenic group have a large ER effect.[8] The mechanism of the large ER effect in the homogeneous polymeric liquid has been interpreted as the inhibition of the slipping between mesogenic domains by the flexible chains connecting them under an electric field. Detailed rheological examinations are necessary for further understanding of the mechanism.

There has been no report on normal stress measurements of ER fluids in spite of its importance in evaluating the rheological property of a material. In particular, this measurement is expected to give us useful information on the structuring of polymer networks which are the basis for the interpretation of the ER effect. In the present paper, unique results have been obtained by measuring normal force under applying/without electric field.

A comb-shaped liquid crystalline polymer[8] (LCP) was supplied by Asahi Chemical Co., Ltd. The LCP was a random copolymer composed of flexible main chain of silicone and flexible side chains connecting mesogens of *p*-cyanophenyl benzoate residue. The mesogen content was 75 weight %. The mesogens have a larger dipole moment along the long axis. The LCP was diluted with dimethyl siloxane (20cSt) at the ratio of 2 : 1 to decrease the initial viscosity. The LCP solution showed smectic phase at room temperature and large viscosity, while it showed isotropic phase at 80°C (Figure 1), suggesting that the mesogens orient in random directions.

A rotating parallel disc type viscometer

---

† To whom correspondence should be addressed.

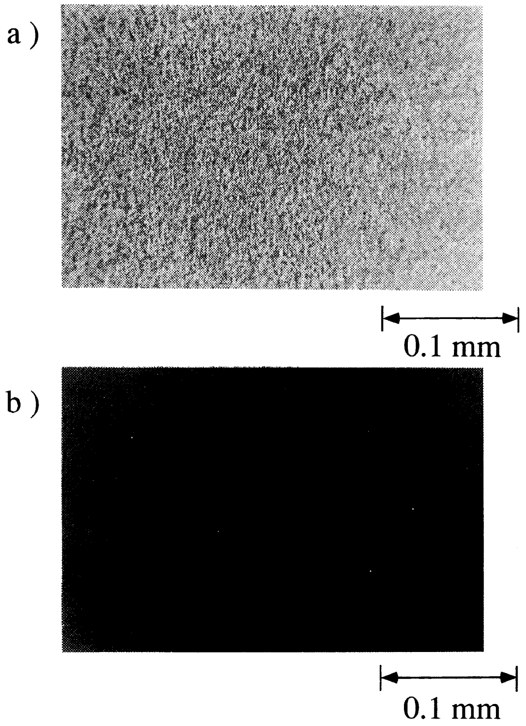

Figure 1. Polarizing micrographs of the LCP (a) at 25°C and (b) at 80°C.

(MR-300, Rheology Co., Ltd.) was used. The two parallel plates play a role of electrodes to apply a homogeneous electric field to the sample fluid. The strength of applied electric fields ranged from $0\,\mathrm{kV\,mm^{-1}}$ to $2\,\mathrm{kV\,mm^{-1}}$. The diameter of the two parallel discs was 32 mm and the gap between the electrodes was 1 mm. In this measurement system, a positive stress value indicates the stress to extend the gap between the discs.

Prior to the rheological measurements, the effect of electric field on the normal force was examined without shear by measuring the stress for the following conditions; (i) no sample, (ii) silicone oil, and (iii) LCP, was respectively placed between the parallel discs. For each condition the normal force under electric field was negative and the absolute value of stress change was in proportion to the square of electric field strength. It is clear that the apparent negative values of normal stress are directly related to the electrostatic force. Therefore, the normal stress measurements under an electric field should be performed taking into account the electrostatic effect on the stress data. Since the shift of stress value scales as the square of the field strength, the stress values can be corrected by subtracting the electrostatic force.

For the evaluation of the strain and shear rate, we used the values at the edge of the parallel discs because these values vary with the distance from center of rotation. Normal stress in the steady shear was measured in the presence and absence of electric field. The stress was determined with the following simplified equation without correcting for the inhomogeneous shear.

$$\Delta n_1 = \frac{2F}{\pi R^2} \qquad (1)$$

Here Δn_1 is the primary normal stress difference, F the thrust, and R the radius of the parallel discs. The Δn_1 value calculated from eq 1 is, thus, not the precise primary normal stress difference but it is a simple estimation for the force normal to the parallel discs.

The discs were rotated at a constant rate to give a shear to the fluid. The shear rate, which is defined here as that at the edge of the discs, was in the range between 10^{-1} and $10^{3}\,\mathrm{s^{-1}}$. The measurements were carried out at 80°C. Figure 2 shows the normal stress measured under 0—$2\,\mathrm{kV\,mm^{-1}}$ electric field. The values under the electric field was corrected for the effect of electrostatic attractive force between the electrodes. Without electric field, the normal stress is almost zero at all shear rates. This result is due to the little normal stress effect of the isotropic LCP. Under the electric field, no change of the stress value is seen at low shear rate region, while at higher shear rates above $10^{1}\,\mathrm{s^{-1}}$, the normal stress increases with the increase of shear rate. The difference of field strength has apparently little effect on the stress values, indicating that the ER effect on the normal stress is almost saturated at

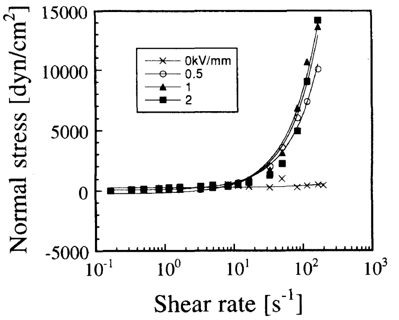

Figure 2. Normal stress vs. shear strain rate under no electric field and under 0.5, 1, and 2 kV mm^{-1} electric field at 80°C. The stress in the presence of electric field was corrected for the effect of electrostatic attractive force.

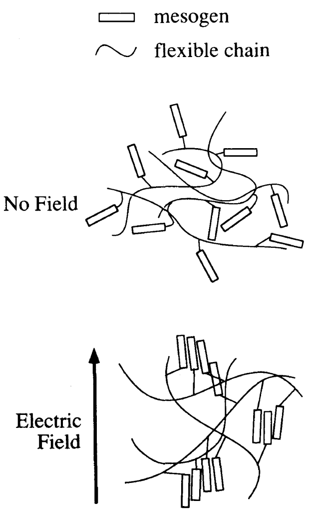

Figure 3. Schematic representation of the possible mechanism for the generation of ER effect in LCP.

around 0.5 kV mm^{-1}. The rapid increase of normal stress at high shear rate region shows existence of entanglements of polymer chains[9] under the field.

The mechanism of ER effect in LCP has been discussed by Inoue on the basis of the comparison of two LCP's having the mesogenic group at one terminal and at both terminals.[8] The bi-terminal LCP showed much higher ER effect than the single-terminal LCP, indicating the flexible chains connecting the LC domains play a significant role in the generation of remarkable ER effect in LCP. Our result of the normal stress measurements demonstrates the existence of induced network structure of polymer chains even though the LCP is isotropic at 80°C. Therefore it is plausible that the electric field affects the orientation of mesogens to form ordered LC domains at this temperature. This result supports the previous interpretation on the mechanism of the ER effect in LCP. A model for the segmental orientation and aggregation under an electric field is schematically illustrated in Figure 3.

In conclusion, it has been clarified that the ER effect of the comb-shaped LCP is based on the network structure induced by the electric field. It has also been demonstrated that the electrorheological normal stress measurement is useful as a new method for evaluating the ER effects.

Acknowledgments. We wish to thank Dr. Akio Inoue (Asahi Chemical Co., Ltd.) for providing the liquid crystalline polymer. This work was partly supported by the Grant-in-Aid from the Ministry of Education, Science and Culture, Japan.

REFERENCES

1. H. Block and J. P. Kelly, *J. Phys. D., Appl. Phys.*, **21**, 1661 (1988).
2. C. Jordan and M. T. Shaw, *IEEE Trans. Electr. Insul.*, **24**, 849 (1989).
3. K. Koyama, Ed., Application & Development of Electro Rheological Fluid [in Japanese], CMC Co. Ltd., Tokyo, 1994.
4. W. M. Winslow, *J. Appl. Phys.*, **20**, 1137 (1949).
5. T. Honda and T. Sasada, *Jpn. J. Appl. Phys.*, **16**, 1775 (1977).
6. T. Honda, T. Sasada, and K. Kurosawa, *Jpn. J. Appl. Phys.*, **17**, 1525 (1978).
7. K. Tanaka, A. Fujii, and K. Koyama, *Polym. J.*, **24**, 995 (1992).
8. A. Inoue and S. Maniwa, EP 478, 034A (1992); to appear in *J. Soc. Rheol. Jpn.*
9. J. D. Ferry, Viscoelastic Properties of Polymers, 3rd ed., Wiley, New York, 1980, Chapter 5.