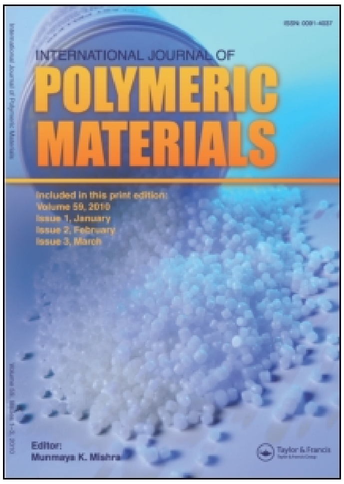

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Manufacture of Films Displaying Liquid-Crystalline Structure

V. E. Gul[a]; O. A. Sdobnikova[a]; A. L. Peshehonova[a]; L. G. Samoilova[a]; O. A. Khanchech[a]; A. I. Suvorova[a]
[a] Moscow Institute for Applied Biotechnology, Dept. of Biotechnology and Polymer Processing, Moscow, Russia

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Manufacture of Films Displaying Liquid-Crystalline Structure

V. E. GUL', O. A. SDOBNIKOVA, A. L. PESHEHONOVA, L. G. SAMOILOVA,
O. A. KHANCHECH and A. I. SUVOROVA

*Moscow Institute for Applied Biotechnology, Dept. of Biotechnology and Polymer Processing,
ul.Talalikhina 33, 109818 Moscow, Russia*

An attempt to attain orientation of macromolecules during extrusion of films of cellulose derivatives that lead to the liquid-crystalline state of a polymer and result in enhanced film strength is reported.

KEY WORDS LC state, orientation, extrusion, cellulose derivatives.

INTRODUCTION

Realization of liquid-crystalline state and orientation of rigid-chain macromolecules have provided a substantial enhancement of the mechanical properties of fibers.[1] It appeared a worthwhile study to make use of the LC ordering when manufacturing film materials.

Mesophases were discovered in solutions and melts of a number of cellulose derivatives, in particular cellulose esters with high degrees of substitution.[2] These observations gave grounds to suggest that systems comprising cellulose diacetate (CDA) and a good plasticizer may, under favorable conditions, exhibit tendency to ordering.

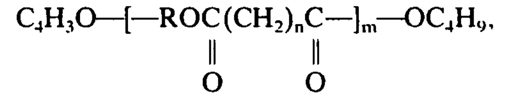
No earlier attempts to detect a liquid-crystalline state in cellulose diacetate plasticized with triacetin (TA) were reported. The other aspect supporting our interest to these systems is related to the need for strong films with a balanced complex of properties for packaging of fatty foodstuffs. Because of the constant exhaustion of the natural feedstocks (naphtha, gas) the ever-growing demand of the food industry for polymeric packaging materials will have to be met by using reproducible natural resources.

The objective of the present study is to obtain insight into the structuring process in CDA-TA and CDA-TA-oligo(ether/ester) systems in order to specify the conditions leading to LC ordering during film manufacture.

RESULTS AND DISCUSSION

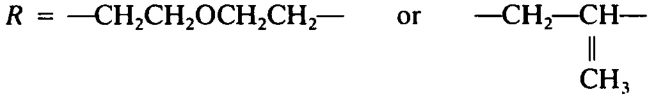
To begin it is worth recalling that only low-substitution cellulose diacetate polymers may be used in acetyl cellulose-based plastics processed by such procedures as injection molding, and extrusion and extrusion blow molding at moderate temperatures (180–200°C). For the polymer specified a plasticizing system had to be chosen that, while decreasing T_g and enhancing segmental mobility, would lead to an equilibrium LC state in the CDA-plasticizer blend.

Cellulose diacetate with 55.8% acetate functions content and a viscosity-average molecular weight 45,000 (measured in acetone) was plasticized with triacetin. Dibutyl (ether/ester)s of the general formula



$$C_4H_3O\text{—}[\text{—}RO\underset{\|}{\overset{}{C}}(CH_2)_n\underset{\|}{C}\text{—}]_m\text{—}OC_4H_9, \quad \text{with } \underset{O}{\overset{\|}{}}\ \text{on both C}$$

where



$$R = \text{—}CH_2CH_2OCH_2CH_2\text{—} \quad \text{or} \quad \text{—}CH_2\text{—}\underset{\underset{CH_3}{\|}}{CH}\text{—}$$

were used as modifiers to the plasticizing system. Specifically, these were dibutyl (ether/ester)s of polyethyleneglycol adipinate, sebacinate, adipinate-sebacinate (PDEA, PDES, PAS-22), and dibutyl ether/ester of polypropyleneglycol adipinate (PPA-4). Within the plasticizing system TA-oligo(ether/ester) the amount of modifier was varied from 0.1 to 10 weight parts, whereas the total amount of the composite plasticizer was constant at 35 weight parts per 100 weight parts of a polymer. The ingredients were mixed for 12 minutes at 293 K in a high-speed turboblender. The blend was homogenized in an extruder-plasticator, with the temperature of the melt at the extruder die head at 453 K. The strands were cooled and cut into granules which were used to produce a continuous film with a slot die extruder; the temperature distribution over the zones of the cylinder was 438-451-468, the temperature of the die was 468, and the inlet temperature was 453 K. The final film thickness was 0.03 cm. The samples used to perform the tests were cut along and across the film length. Thin CDA-TA-oligo(ether/ester) films (20 μm) were prepared by hot pressure molding at 423 K and 12 MPa.

Phase transitions in plasticized compositions were registered refractometrically with a URL-1 refractometer by measuring the temperature dependence of the refractive index of thin films (20 μm) at a continuous temperature variation rate of 1 K/min; X-ray diffraction analysis was also used as the alternative method. Glass transition temperature (T_g) was determined thermomechanically at constant stress (1.4 10^{-2} Pa) and at a continuous temperature variation rate of 1 K/min or refractometrically. Both procedures were shown to give consistent results.

Mechanical properties of extruded films were examined with an Instron testing machine in accord with the requirements of the State Standard GOST 14236-81; the testing temperatures were 293 and 393 K, the strain rate was 10^{-2} m/h, and the working area of the samples subjected to testing was $(5 \times 10 \times 0.3)\ 10^{-3}$ m^3.

Rheological properties of the material were investigated with a capillary viscometer at constant pressure at 453 and 483 K; the shear rate varied from 10^{-3} to 10^4 s^{-1}.

To define the region in which cellulose diacetate was in the mesomorphic state, temperature and concentration conditions leading to LC-phase in the system involving complex triacetin-oligo(ether/ester) plasticizer were examined by polarization microscopy, light transmission measurements, small-angle light-scattering of polarized light, and X-ray diffraction analysis.

When investigating the phase state of the systems specified, a rather narrow region of phase segregation was discovered[3] (outlined by the dashed line in Figure 1) which correlated with the theoretical predictions made by Papkov *et al.*[4] for a solution of semi-rigid macromolecules of the like structure.

Anisotropic melts of plasticized cellulose diacetate were highly viscous and exhibited a characteristic pearly sheen, which disappeared on heating and returned on cooling. Light-scattering diffraction patterns from samples with different plasticizer content reveal an overall anisotropy of the system associated with the mesomorphic transition to the LC state taking place during film production (Figure 2). As illustrated, H_v-scattering-pattern of polarized light appears to be positioned

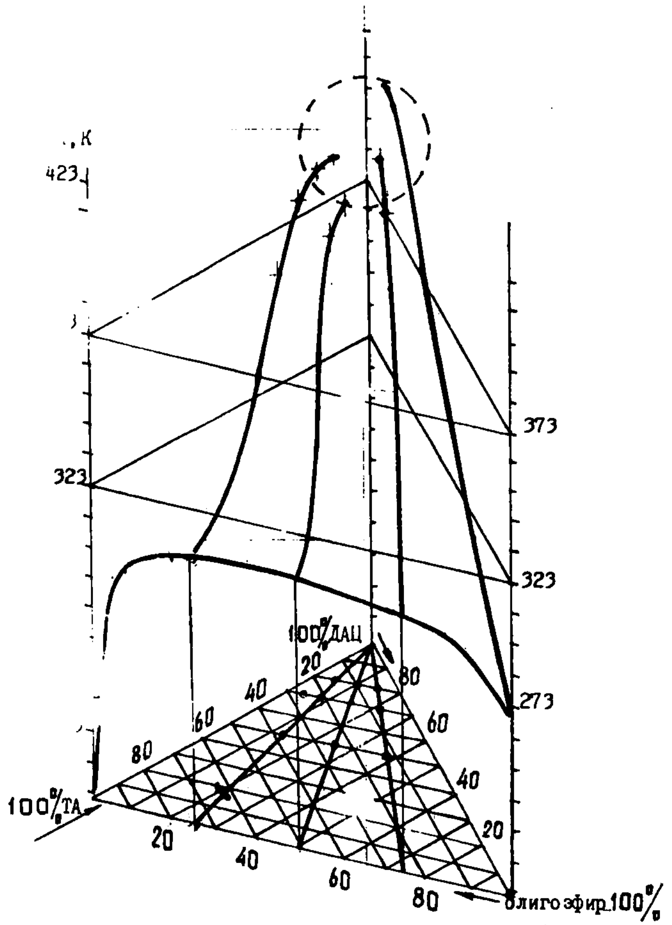


FIGURE 1 Three dimensional phase diagram of the ternary system CDA-TA-oligo(ether/ester).

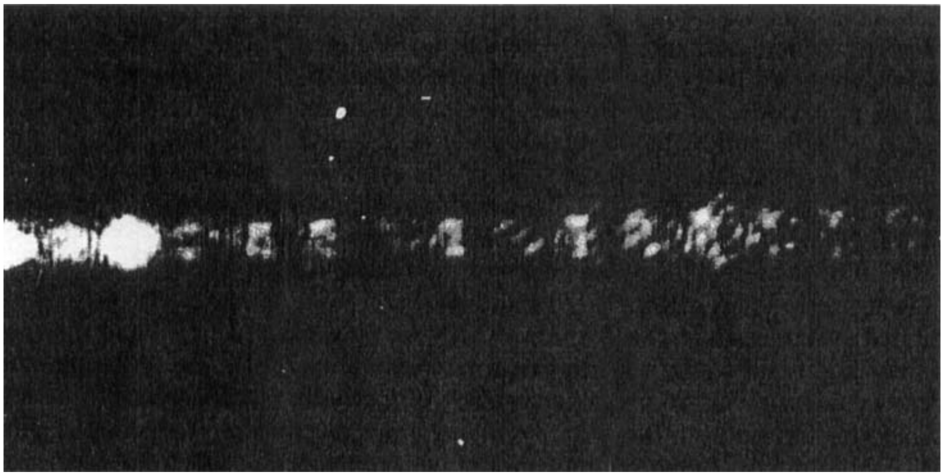


FIGURE 2 H_v-pattern of small-angle scattering of polarized light by the melt of plasticized CDA.

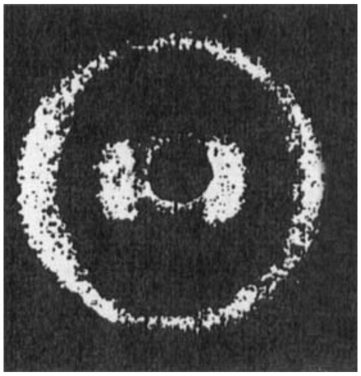


FIGURE 3 X-ray diffraction pattern of CDA containing 45% plasticizer.

perpendicular to the strain direction. The pattern displays periodicity manifested as distinct diffraction maxima at azimuthal angles 0 and 180°. Such scattering patterns were reported earlier by Rhodes and Stein[5] for the films of synthetic polymers; they were interpreted as resulting from light scattering by rod-like structures whose polarizability axis lies at an angle of 45° to the rod axis. The dependence of the intensity of H_v-patterns on azimuthal angle is most often observed in light scattering from cholesteric liquid crystals.[6] Figure 3 shows the X-ray diffraction pattern of CDA containing 45 weight% plasticizer. The optical activity of the system is verified by the retention of the interferential coloration of the quenching pattern when the microscope table is rotated,[7] a feature characteristic of cholesteric liquid crystals. Crystalline ordering during film production obviously should lead to increased film strength.[8]

In order to clarify the mechanism of the strengthening effect of a good plasticizer at its high concentration the structure of plasticized low-substitution CDA was investigated. Electron microscopy disclosed that the samples prepared from ther-

FIGURE 4 Electron micrograph of the sample prepared from thermotropic melt of plasticized CDA. Magnification ×72,000.

motropic melt at 453 K reveal a stranded structure which appears to be one of the structural and morphological features characteristic of the LC-state in CDA (Figure 4).

According to the optical studies with polarized light at 453 K the transition of plasticized CDA melts to the LC-state takes place at TA concentration around 35 weight%. The flow curve patterns support this observation. For instance, within the initial range of the shear stress τ CDA melts containing 25 weight% TA essentially behave as Newtonian (Figure 5). Increasing the TA content substantially affects the lg η vs. lg τ dependence pattern. Three regions are distinguishable in the flow curves. In region I, encompassing lg τ values from 5.7 to 5.8, an abrupt decrease of lg η accompanies the increase of the shear stress (Figure 5, curve 2). Such a viscosity variation pattern is common when rigid linear kinetic units are oriented during flow. An actually complete orientation of rigid "rods" along the flow direction results in the decrease of lg η down to 5.1. Subsequent increase of the shear stress does not noticeably affect the viscosity coefficient. The melt performs as a Newtonian fluid with a practically constant magnitude of the viscosity coefficient. However, along with the rigid fragments a macromolecule contains relatively flexible fragments with a coiled conformation. At sufficiently high values of lg τ ranging from 5.8 to approximately 5.95 the configurational set of these relatively flexible fragments begins to diminish. This process proceeds through the region II which displays a pattern characteristic of rubber-like deformation accompanied by a decrease in viscosity with increasing τ. After this mechanism is complete

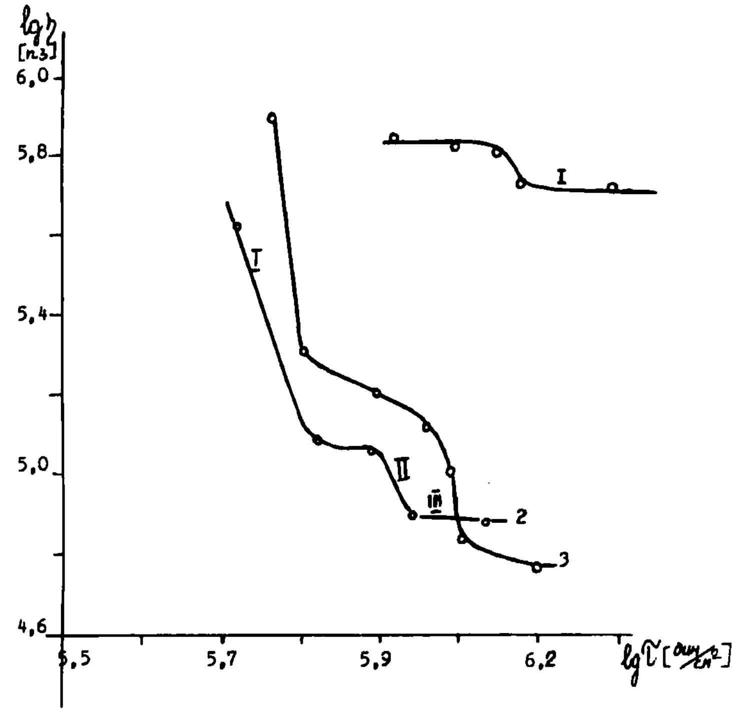


FIGURE 5 Flow curves of the melt of plasticized CDA at 180 C. 1 = 25 weight% TA, 2 = 45 weight% TA, and 3 = 35 weight% (30 TA + 5 PPA).

the flow curve proceeds into region III, quite common for polymeric fluids; here η represents the minimal Newtonian viscosity and becomes independent of τ. CDA melt plasticized with a mixed plasticizer (TA + oligo(ether/ester)) shows a similar dependence. However, the respective curve results from the composition containing 10% less plasticizer. Hence, the composite plasticizer appears to be more effective.

Curve 1 in Figure 5 corresponds to the least added amount of the plasticizer containing no oligo(ether/ester). This system behaves as a conventional polymeric fluid (Reference 9, p. 168). The flat portion of the curve at lg η = 5.8 describes the fluid with high viscosity coefficient, viz. with the maximal Newtonian viscosity η_0. The flow proceeds within the system of rigid anisotropic structures distributed at random. These fragments interfere with each other and, hence, are not liable to get oriented along the flow. Relatively more flexible macromolecular fragments are not likely to vary their conformational set at the shear stress magnitude specified. However, at sufficiently large lg τ values (approx. from 6.0 to 6.1) the shape of the flexible chain fragments tends to be distorted by the stress applied. Within this range of τ values the magnitude of η changes from that of the maximal Newtonian viscosity to that of the minimal Newtonian viscosity, and then actually stays constant within the lg τ range from 6.0 to 6.3, the highest τ value attained in the experiments.

The second feature specific of the rheological properties of LC melts is the unusual pattern of the viscosity vs. concentration dependence, depicted in Figure

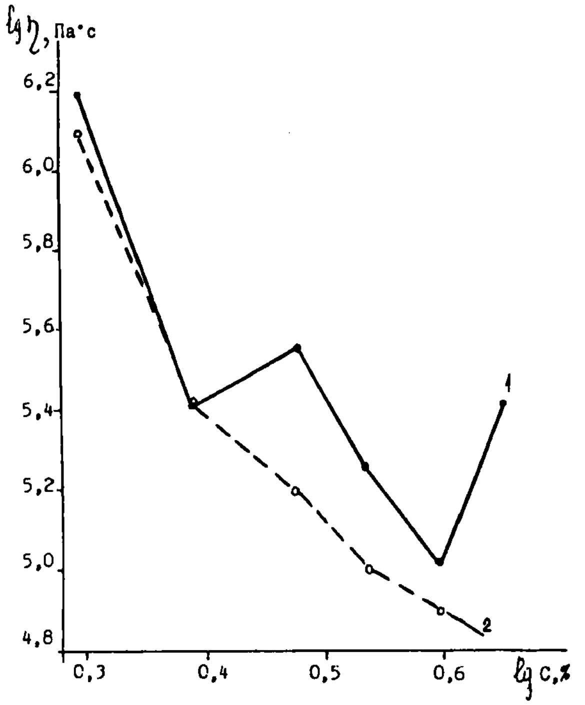


FIGURE 6 Viscosity of the melt of plasticized CDA versus plasticizer content at different τ. 1 = 5.8 pa, and 2 = 6.2 Pa.

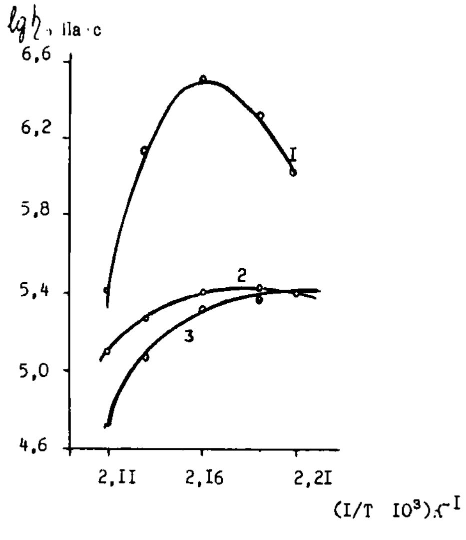


FIGURE 7 Viscosity versus temperature dependences for the melts of plasticized CDA with different plasticizer content. 1 = 25 weight% TA, 2 = 35 weight% TA, and 3 = 45 weight% TA.

TABLE I

Comparison of the properties of conventional cellulose diacetate plastic with those of the plastic with the fixed LC-phase

	Technological characteristics						Service properties		
Material	η 10^5	σ_{20}	ε_{20}	σ_{120}	E 10^4	T_g	M_t/M_0	τ_θ	Volatility of plasticizer
CDA plastic	4.8	40	50	1.4	0.8	180	0.9	up to 72	16
CDA plastic with the LC phase	1.0	70	10	10	2.3	160	0.5	120	3

η = viscosity of the melt at 453 K, poise.
σ_{20} = tensile strength (20 C), MPa.
ε_{20} = relative elongation at break (20 C), %.
σ_{120} = tensile strength (120 C), MPa.
E = modulus of elasticity (20 C), GPa.
T_g = glass transition temperature, C.
M_t/M_0 = relative migration of low molecular weight substances.
τ_θ = service life, h.

6. As shown in curve 1, viscosity can exhibit a substantial upward jump during the transition to the LC state mediated by increasing plasticizer content. Viscosity vs. temperature dependences display maxima in the region corresponding to the transition from isotropic state to anisotropic (Figure 7). We attribute the observed effects to the viscosity anisotropy manifested as the dependence of internal friction on the extent of orientation of the long axes of macromolecules along the direction of flow.[1,2] When the melt is in the LC state the efficiency of intermolecular interaction between macromolecules oriented in parallel increases. In this case it is no longer the hydrodynamic resistance of isolated macromolecules that is important but rather that of macromolecular associates.

To enable the system to pass to the nematic form it is necessary to ensure the high mobility of the components at relatively low plasticizer content. The system undergoes such lyotropic transition more effectively the more powerful in its effect is the plasticizer. The effect of a plasticizer is largely determined by the enthalpy of mixing or, in other words, by the ratio between specific energies of cohesion of a polymer and a plasticizer. For instance, it is well known[10,11] that the swelling of a polymer in a low molecular weight component is higher the lesser the difference is between specific cohesion energies of the components mixed. Gul' and Klitenik[10] discovered that molecular light-scattering of a benzene solution of 1,4-cis-polyisoprene decreases with the addition of small amounts of precipitating solvent (methanol). The observed effect was ascribed to the cohesion energy of the binary solvent being equal to that of the polymer. A similar effect was expected to take place when plasticizing CDA with a mixture of compatible and incompatible plasticizers. When 5 weight% of oligo(ether/ester) is added the cohesion energy of the complex plasticizer approaches that of CDA proper. For instance, cellulose diacetate (δ = 10.9) is soluble in triacetin (δ = 10.5) and poorly soluble in oligo(ether/ester) (δ = 9.6), the introduction of small amounts of oligo(ether/ester) causing the increase in mobility of the system as a whole.

The LC ordering discovered in the CDA-TA-oligo(ether/ester) system was applied when developing cellulose acetate plastics grades for food industry and designing on this basis strong packaging films with tailored performance characteristics. Table I gives a comparison of the properties of the "initial" (conventional) cellulose acetate plastic with those of the plastic with the fixed mesophase. As shown, the mechanical properties of the films obtained in the process leading to the formation of the LC state are substantially better. For instance, the tensile strength σ_{120} of a plastic with fixed mesophase is by an order of magnitude higher than that of the conventional plastic.

CONCLUSION

Hence, it is not only in the manufacture of strong fibers that the orientation and ordering of the structure can be made to attain the perfection of the LC state; this effect is also feasible when preparing films by extrusion. The significant improvement of the characteristics of the cellulose acetate plastic and of the films derived is due to the equilibrium character of the molecular orientation within the material associated with the ordered structure. The results of the study were scaled-up to the pilot plant.

References

1. D. H. Southern and R. S. Porter, *J. Applied Polymer Science*, **14**, 2305 (1970).
2. V. G. Kulichihin and L. K. Golova, *Khimia.Drevesiny*, **3**, 9 (1985).
3. A. L. Peshehonova, A. I. Suvorova, O. A. Sdobnikova and V. I. Andreeva, *Izv. VysShikh Uchebn. Zaved. SSSR, Ser. Khimiya i Khimich. Tekhnologiya*, 11 (1988).
4. S. P. Papkov, Yu. Ya. Belousov and V. G. Kulichihin, *Khimicheskie Volokna*, **3**, 8 (1983).
5. M. B. Rhodes and R. S. Stein, *J. Polym. Sci.*, **A2**, 1539 (1969).
6. T. Hashimo, S. Ebisy, N. Inova and H. Kawai, *Polymer J.*, **13**, 701 (1981).
7. L. G. Shaltyko, A. A. Shepelevskii and S. Ya. Frenkel, *Proceedings of the All-Union Conference on Liquid Crystals*, Ivanova, 121–129 (1979).
8. V. E. Gul', *Polymer Structure and Strength*, Khimiya, Moscow, 295–298 (1978).
9. V. E. Gul' and V. N. Kuleznyov, *Structure and Mechanical Properties of Polymers*, Vysshaya Shkola, Moscow, 352 (1978).
10. V. E. Gul' and G. S. Klitenik, *Kolloidnyi Zh.*, **14**, 171 (1954).
11. G. Gee, *J. Polym. Sci.*, **2**, 451 (1947).