REVIEWS

BASIC TRENDS IN TECHNOLOGY OF MANUFACTURING CELLULOSE FILMS AND CASINGS

V. M. Irklei

Cellulose films prepared for viscose were the first packing materials which found wide application in the food (especially as sausage casings), medicinal, and aviation branches of industry and trade, and for technical purposes. In our country, they have become known under the name "tsellofan (cellophane)." The most vigorous development of cellophane took place between the 40s and 60s where technology was developed for cellophane with coatings based on synthetic polymers: lacquered cellophane appeared as well as doubled bicomponent films of the polyethylene-cellophane type, multilayer film materials such as polyethylene-cellophane foil, one-sided lacquered cellophane-polyethylene, and many other combinations.

In the 60s and 70s, an independent industry of cellulosic casings from viscoses was developed, which is leading to a cutback in cellophane manufacture; since 1974, the output of cellophane has been cut by 60% [1], and demand for its has been determined by the manufacture of heat-sealable lacquered and doubled films. In this same period, films based on polyolefins received wide development and in some cases this was as a replacement for lacquered cellophane, for example, for packaging cigarettes, where biaxially oriented films of polypropylene (PP) and lacquered or coated PP became used.

Therefore, most of the companies in Western Europe and the USA have cut down or ceased production of cellophane due to its low price, high manufacturing costs, and correspondingly, the lack of profit from such plants. Only the BCL company (a division of the "Courtaulds" company of Great Britain) has kept up its manufacturing capacity. Among the countries which are members of the East European Economic Community, the USSR has first place in the manufacture of cellophane. According to the estimate of the International Union of Cellophane Manufacturers, in the European market cellophane and polypropylene have approximately equal shares, while in the USA and Japan, polypropylene has become the basic packaging material [2]. However, cellulosic films have continued to be irreplaceable packaging materials thanks to a number of properties such as a high degree of transparency, flexibility, elasticity, and reasonable strength. Moreover, in distinction from other polymeric synthetic films, cellulosic films do not accumulate static electrical charges and have the ability to be degraded by biological means. This latter property is very important in connection with the increase in amount of household waste and the need for utilizing it [3, 4].

In machined processing, cellophane has important advantages as compared with other film-forming materials. Therefore, as before, over 100 forms of cellophane film are used in various branches of industry: from packaging chocolate articles to decorating panels of plastics [5]. In recent times, measures have been undertaken to modify cellophane by various technological devices, to give new properties and create a new assortment, for example, by decorative embossing, metallization, doubling, or lamination. Specialists have been concerned with continuous improvement of the viscose process using the latest technology, microprocessors, and high-quality raw materials.

In distinction from cellophane, the demand for cellulosic casings for food products has not been decreasing. This is explained by the fact that up to the present, no alternative material from synthetic polymers has been developed. Cellulose casings for making sausages on high productivity equipment are the basic packaging material; their development in the USSR which has an adequately prepared raw material base is very promising.

Let us examine some problems associated with the manufacture of cellulose films and casings.

As is well known, the preparation of spinning solutions and the composition of the viscose largely determine the technical-economic and ecological indices of processes for preparing hydrocellulose films and casings. The basic problem in manufacturing them is to increase the quality of the spinning solutions at a minimum consumption of sodium hydroxide and

especially of the toxic material carbon disulfide. The search for ways to reduce the consumption of carbon disulfide is an urgent problem; the fate of the viscose method of preparing cellulosic materials depends on success in solving it. Therefore, a cycle of studies is being carried out in the Kiev branch of the VNIIVproekt, aimed at a search for new means of increasing the reactivity of cellulosic products.

Some traditional methods of increasing the reactivity of cellulose are well known: those using surface-active substances, ammonia, or various amines or amides. The effect of these on structural changes in cellulose has been analyzed in detail in [6]. The most widely available and effective substance has turned out to be urea, introduction of which into the dissolving alkali during xanthation aids in obtaining cellulose xanthates with a high degree of xanthation at a reduced consumption of carbon disulfide. The technology of such a process is given in [7]. An increase in the reactivity of cellulose is observed when its molecular weight nonuniformity is reduced, as may be evaluated by the polydispersity index $\overline{DP}_w/\overline{DP}_n - 1$, where $\overline{DP}_w$ and $\overline{DP}_n$ are the weight average and number average degrees of polymerization of the cellulose. For these purposes, the radiochemical method of [8] is most effctive. By using it, it is possible to considerably reduce molecular weight nonuniformity and to obtain celluloses having a DP required for technological processes without changing essentially the degree of crystallinity or the content of low-molecular-weight fractions. Below, we give data on the change in polydispersity index in a starting cellulose after depolymerization of the alkali cellulose and in the final film:

Cellulose	Original cellulose	Depolymerized cellulose	Cellulose film
Tirpcord	0,59	0,33	0,32
Silk-like	0,51	0,29	0,27
Cotton of the "Bakai" company	0,33	0,25	0,22
Cotton manufacture in the USSR	0,31	0,22	0,21

From the data presented, it is evident that the polydispersity of cellulose decreases after depolymerization of the alkali cellulose and is essentially retained in the finished material. On γ-irradiation of tire-cord cellulose with a dose of 10 kGy, the polydispersity index is reduced to 0.1 and is maintained over the course of the entire cycle of film preparation. Below, we give data on the filterability of viscoses prepared from celluloses with various polydispersity indices, which were evaluated by the $\overline{DP}_w/\overline{DP}_n - 1$ index; the filterability of the viscoses was evaluated by the K_W index:

$\overline{DP}_w/\overline{DP}_n - 1$	K_W	$\overline{DP}_w/\overline{DP}_n - 1$	K_W
0,33	380	0,22	150
0,29	270	0,10	70
0,25	220		

In preparing the viscoses, the consumption of carbon disulfide was 32-33% of the weight of the α-cellulose.

The changes which take place in the ordered (crystalline) regions of the cellulose play the decisive role in preparing viscoses with good filterability [9-11]. A study of the crystallographic relationships in forming inclusion compounds of the alkali metal hydroxides with cellulose, the phase transitions in mercerization, and the crystal chemistry features and stoichiometry of the hydrated cellulose xanthates have made it possible to establish a method for calculating optimum concentrations in cellulose mercerization and to represent the mechanism for xanthation in the alkali cellulose crystallites. In the indicated researches, structural transformations of celluloses were evaluated from the change in the interplanar distance $d_{101}{}^a$ in the alkali celluloses and $d_{101}{}^x$ in the xanthate. A rather clear connection can be traced between the changes in the alkali cellulose crystallites and the cellulose xanthate, the consumption of carbon disulfide, and the filterability of the viscoses. Below, we give the values of $d_{101}{}^a$, maximum values of $d_{101}{}^x$ in the lattice of the cellulose xanthate, the minimum values of carbon disulfite consumption at which they are formed during the process of esterification, and the K_W of the viscoses prepared from these xanthates:

d_{101}^a, Å	d_{101}^x, Å	Consumption of CS_2, %	K_W
12,8	14,5	35	200
13,2	15,5	32	190
14,0	17,5	25	180
15,0	25,0	22	100

As is evident from the data presented, the greater the interplanar distance in the crystalline lattices of the alkali cellulose and in the cellulose xanthate, the less carbon disulfide is necessary for preparing viscoses having high filterability for which K_W is in the range 100-200 arbitrary units.

Thus, reducing the polydispersity of the cellulose and selecting optimum conditions for mercerization, the composition of the alkali cellulose before xanthation will make it possible to realize technology for preparing viscoses with a carbon disulfide
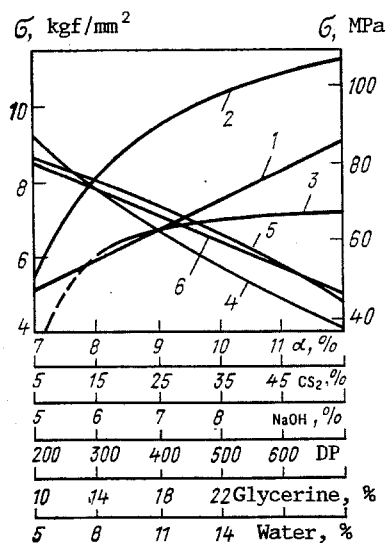
σ, kgf/mm^2 σ, MPa

10   100

8   80

6   60

4   40

7   8   9   10   11 α, %

5   15   25   35   45 CS$_2$, %

5   6   7   8   NaOH, %

200 300 400 500 600 DP

10   14   18   22 Glycerine, %

5   8   11   14 Water, %

Fig. 1. Dependence of strength of isotropic films on the composition of the viscose and of the film: 1) α-cellulose content, % by wt.; 2) DP; 3) CS$_2$ content, % on weight of α-cellulose; 4, 5, 6) NaOH content, glycerine content, and water content, % by wt.

consumption of 15-20% by wt., as is supported by experiments under pilot plant conditions. However, the preparation of films from viscoses having a low degree of esterification has its own peculiarities, for which it is necessary to investigate the effect of the basic viscose indices and composition of the film on its strength characteristics.

In Fig. 1, we show the effect of α-cellulose content, sodium hydroxide content and that of carbon disulfide, glycerine, moisture and the DP of the cellulose on the tension at break (σ) of isotropic cellulose films prepared by biaxial orientation. A linear rise in breaking tension is observed with increase in the polymer content of the spinning solution (curve 1). An increase in σ takes place also on increasing the DP of the cellulose in the films (curve 2) to values of approximately 500. Further increase in DP shows up to a smaller extent. At a carbon disulfide content in the viscose of less than 20% by wt., an abrupt decrease in the strength of the films is observed (curve 3). The strength of cellulose films and casings is reduced on increasing the sodium hydroxide content of the viscose (curve 4), or that of glycerine (curve 5), or water (curve 6) in the films. From the data given, it follows that it is necessary to compensate for the loss in strength of films prepared from viscoses having a reduced carbon disulfide content by changing other parameters of the viscose and the content of plasticizers.

Knowledge of the principles involved in regulating the strength properties is especially important in making cellulose films of thickness 9-15 μm, which are used as membranes. Cellulose membranes, whose manufacture has been developed under industrial conditions, are being used successfully for dialysis, in particular for hemodialysis, ultrafiltration, and separating substances of different molecular weight, and for other purposes. The properties of domestic membranes for hemodialysis, "diatsell" and "ul'tratsell," are given below:

| Property	Diatsell	Ul'tratsell
Thickness, μm	15.5±1.5	15.5±1.5
Breaking tension in stretch, MPa:		
in lengthwise direction, not less than	63.7	63.7
in transverse direction, not less than	29.4	29.4
Glycerine content, % by wt.	20-25	20-40
Actual moisture content, %	3.5-1.0	3.5-7.0
Rate of water ultrafiltration at 20°C, ml/(min·cm^2·kPa)	$(3.2\text{-}4.5)\cdot10^{-5}$	$(4.5\text{-}10.0)\cdot10^{-5}$
Dialysis permeability constant at 37°C, cm/min:		
with respect to urea	$(48\text{-}64)\cdot10^{-3}$	—
with respect to vitamin B$_{12}$, not less than	—	$7.0\cdot10^{-3}$

183
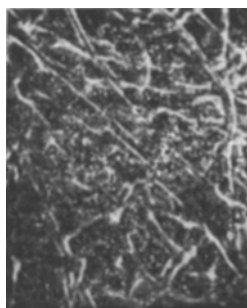
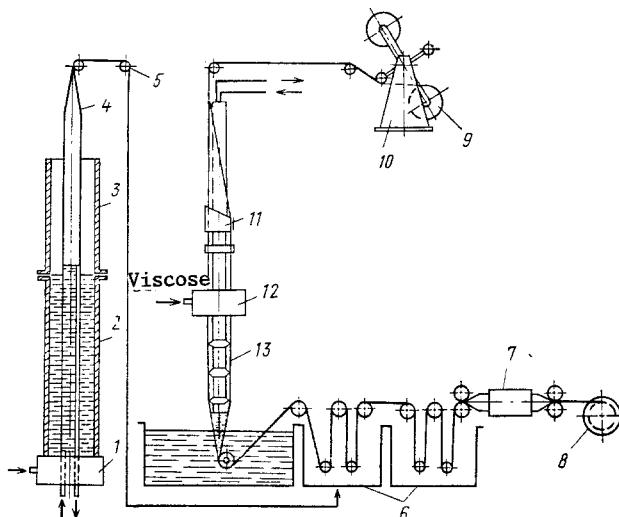Fig. 2. Microphotograph of a structure of a reinforced casing (10×).

Fig. 3. Technological scheme for the preparation of seamless and reinforced casings: 1) device for shaping; 2) spinning tube; 3) vertical chamber; 4, 13) casing; 5) take-up drum; 6) reservoirs for final regeneration of the casing; 7) dryer; 8, 9) rolls; 10) mechanism for unwinding paper tape; 11) device for giving tape the shape of a tube; 12) spinneret.

Membranes made of cellulose can be used successfully to separate not only liquids but also gases. Below we give data on the permeability of various gases (P) through cellulose membranes containing 24% by wt. of a plasticizer (glycerine) and 14% water:

Gas	$P \cdot 10^{10}$, $\dfrac{cm^3 \cdot cm}{cm^2 \cdot sec \cdot cm\ Hg}$	Gas	$P \cdot 10^{10}$, $\dfrac{cm^2 \cdot cm}{cm^2 \cdot sec \cdot cm\ Hg}$
NH_3	29386	H_2	0,0895
SO_2	82,441	O_2	0,0319
CO_2	0,955	N_2	0,0071

The gas-permeability of cellulose membranes is largely determined by the solubility of the gases in water. Therefore, cellulose membranes are very effective for easily-soluble gases, particularly ammonia, and their permeability may be regulated over wide ranges by the plasticizer content and the moisture content.

However, a definite assortment of cellulose films should have a high permeability to water vapor and to fumes while preserving a high elasticity and thermal resistance. Primarily, this relates to cellulosic casings, which are used to make sausages of various assortments. Three main kinds of casings are used both in the USSR and abroad for the manufacture of various sausages: seamless and reinforced viscose, artificial protein, and polymer [12]. Thanks to the availability of the starting raw material and the practically unlimited reserves in it, hygienic transparent and shiny seamless casings have successfully retained their position in the world market. They are used mainly for packaging cooked sausages.

The technological cycle for making half-smoked and smoked sausages, which is carried out under conditions of high humidity and a high temperature difference is longer. To make them, casings are required which have a high transparency in the moist state, the so-called "reinforced casings." They are a composite consisting of regenerated cellulose and highly crystalline (crystallinity index X_c = 0.7-0.76), high-molecular natural fibres such as cotton, manila help, linen, or others. The structure of such casings is evident in the photograph of the internal surface of a reinforced casing (Fig. 2).

In Fig. 3, we give the technological scheme for spinning seamless and reinforced casings.

Preparation of a seamless casing is carried out on a flow line as follows. Viscose having assigned indices passes through a device for shaping 1 into the spinning tube 2. The construction of the device for shaping is carried out in such a way that a casing which has been shaped in the form of a hollow cylindrical tube is subjected to the action of a precipitation bath both on the inner and outer sides. The "internal" precipitation bath is delivered into the space between the tube and the casing being shaped. The casing 4 is transported into a vertical chamber 3, and is guided onto the take-up drum 5. After this, the casing passes to the finishing section of the flow line, which consists of reservoirs 6 in which final regeneration of the casing is carried out plus desulfurizing, washing, and plasticizing. Moisture is removed from the casing in the dryer 7, and the finished casing is wound on roll 8.

A reinforced casing is obtained upon impregnation of a viscose paper base, consisting as indicated previously of natural fibres. To do this, the paper base passes from roll 9 of a mechanism for unwinding paper tape 10 into device 11 for giving the tape the form of a tube, and then is routed to the spinneret 12 for impregnation with viscose. After this, the casing 13 is treated with a precipitation bath from inside and outside. Subsequent technological operations are analogous to the operations in preparing seamless casings.

To give cellulose casings a natural appearance, they are colored with lignin, which is introduced into the viscose. Moreover, by introducing lignin into the viscose, it is possible to vary within wide limits the light-protective properties of the casings, which makes it possible to protect sausages from changes which take place as a result of oxidative processes under the influence of light [13]. Below, we give data about relative light absorption, calculated as partial absorption of UV radiation by lignin colored and uncolored, colorless casings as a function of the lignin content of the viscose:

Lignin content, % of wt. of α-cellulose	Light absorption at wavelength, nm, of				
	210	260	280	300	320
2	2,3	1,9	1,8	2,26	2,3
4	3,2	4,3	4,2	4,6	4,3
6	9,1	7,3	7,1	7,6	6,9
8	10,3	12,4	13,8	13,3	12,7
10	P	P	17,5	16,9	17,2
12	P	P	P	17,3	17,7
14	P	P	P	17,8	18,1

Note. P denotes total absorption.

To reduce the vapor permeability of films and casings, to stabilize their dimensions and form under conditions of various humidities and temperatures, and to give them the ability to be heat sealed on high-speed automatic packaging machines, the indicated material is coated with lacquers based on nitrocellulose, vinyl chloride copolymers (VCVD-40), or polyvinylchloride. Application of these coating compositions is carried out on coating units using toxic organic solvents, for whose removal and regeneration in the cycle special recovery units are required [4]. The use of such installations in viscose manufacturing units significantly impairs the ecological situation. Therefore, methods of applying coating compositions based on aqueous dispersions of vinyl chloride copolymers (VCVD-65, CVC-1) are being developed.

Experimental technology has been developed in the Kiev branch of the VNIIVproekt, and work is being conducted on development of special equipment to carry it out. Below, we give some data on the vapor permeability of cellulose films 30 μm thick without a coating and with a coating surface density of 2.5 g/m²:

Type of coating	Vapor permeability in 24 h, g/m²
None	350
Nitrocellulose	27
Aqueous dispersion of VCVD-65B	22
Aqueous dispersion of CVC-1	24

With the objective of improving the adhesion of cellulose films to the coating compositions, their surface is modified with adhesives, for example, with melamine-formaldehyde (MF) resin. Along with increasing adhesive strength, the strength of the heat seal is increased in the coated films, which is the basis for processing them on high-speed equipment. Schemes for the
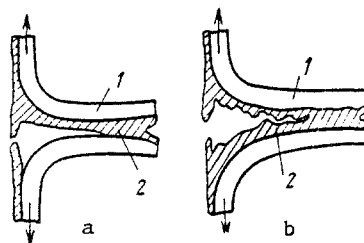
Fig. 4. Failure scheme of a heat-seal seam of lacquered films without an adhesive (a) and with an adhesive (b); 1) cellulose film; 2) with lacquer coating.

failure of heat-sealed seams with an adhesive and without it are shown in Fig. 4. Below, we give values for the optimum sealing temperature and also for the seal strength of coated films with various polymer coatings with application of MF resin and without it:

	t, °C	Seam strength, g/cm
Nitrocellulose lacquer	125±5	80
Same + MF	125±5	110
VCVD-40 lacquer	145±5	50
Same + MF	145±5	130
Aqueous dispersion of CVC-1	145±5	36
Same + MF	145±5	153
Aqueous dispersion of VCVD-65	145±5	50
Same + MF	175±5	160

Films which have been coated on just one side with the indicated lacquers in dispersions can be used successfully to make combined film materials.

CONCLUSIONS

Basic directions of work in the region of manufacturing cellulose films and casings have been defined:

— improvement in existing technological cellophane manufacturing operations and operations for producing coated films based on it;

— organization of domestic manufacture of viscose casings using low waste, ecologically safe technology;

— modification of the properties of cellulosic films and casings with the objective of preparing membranes for various purposes;

— expansion of the assortment of combined film materials based on cellulosic films.

LITERATURE CITED

1. J. Brasier, Pap., Film and Foil Converter, 62, No. 8, 48-52 (1988).
2. Vl. Kacvinsky, Chemicke Vlakna, 35, No. 4, 275-282 (1985).
3. M. Szewezyk, Folia Celulozowa-Tomofan, Opakonia, No. 1, 4-9 (1989).
4. Cellophane Alone in a Plastic Crowd, Paska—Ging (USA), 32, No. 14, 89 (1987).
5. J. Brasier, Mates. and Des., 7, No. 2, 65-67 (1986).
6. A. Sh. Goikhman and V. P. Solomko, High-Molecular Inclusion Compounds [in Russian], Naukova Dumka, Kiev (1982).
7. V. M. Irklei, L. V. Ostapets, et al., Khim. Volokna, No. 5, 46-48 (1986).
8. A. K. Stavtsov, A. P. Meleshevich, V. M. Irklei, et al., Khim. Volokna, No. 2, 22-23 (1988).
9. A. Sh. Goikhman, M. Ya. Ioelovich, and V. M. Irklei, Khim. Drevesiny, No. 4, 7-11 (1986).
10. V. M. Irklei and A. Sh. Goikhman, Vysokomol. Soed., Ser. A, 29, No. 12, 2467-2472 (1987).
11. V. M. Irklei and A. Sh. Goikhman, Khim. Volokna, No. 1, 5-9 (1988).
12. A. A. Dergunova and N. N. Shishkina, Sausage-Casing Manufacturing Technology [in Russian], Pishch. Prom-st', Moscow (1973).

13. R. K. Smirnova, N. F. Zaitseva, V. M. Irklei, et al., Investigation of the Mechanical and Technological Characteristics of Domestic Seamless Cellulose Casings for Sausages. A Collection of Scientific Works [in Russian], VNIIMP, Moscow (1985), 30-36.

14. V. M. Irklei, L. P. Sharai, et al., Hydrophobization of Hydrocellulose Films [in Russian], NIITÉKhIM, Moscow (1986).

HIGH-STRENGTH HIGH-MODULUS FIBRES FROM LIQUID-CRYSTALLINE AROMATIC POLYESTERS

A. V. Volokhina

Fibre-forming liquid-crystalline (LC) polyesters are a new generation of highly efficient polymers. They were synthesized in the middle of the 70s, that is, approximately ten years after the preparation of LC aromatic polyamides. Industrial manufacture of the latter in the preparation of high-strength fibres based on them, of the Kevlar type, was organized at the start of the 70s. LC polyesters became commercial products at the start of the 80s, that is, also about ten years after their first preparation.

At present, the capacities for production of aromatic polyesters with the trade names Xyder and Vectra in the United States, intended mainly for use as high-strength and heat-resistant constructional plastics, are about 10,000 and about 4500 tons per year, respectively. Many companies in Japan, West Germany, Great Britain, and other countries are developing the production of liquid-crystal polyesters in experimental or industrial volumes (with the trade names Ekonol, Ultrex, X7G, Rodran, and so forth). As concerns fibres, these are being prepared so far on the scale of small experimental lots under the trade names Ekonol, Vektran, and Xydar.

A significant advantage of high-strength fibres from liquid-crystal polyesters as compared with analogous polyamide fibres is the possibility of using the very economical and ecologically clean method of melt spinning. The thermoplasticity of polyester fibres affords the possibility of using them as highly oriented binders for the preparation of extremely highly reinforced composite materials. This explains the great interest which is displayed by specialists of various types in high strength fibres from liquid-crystal polyesters. In distinction from the latter, liquid-crystals of polyamides do not melt up to the decomposition temperature and go over into an ordered LC state only in solution. These lyotropic polymers are very difficult to process into constructional articles of complex configuration; therefore, fibres or films are mainly prepared from them.

Transition of the structure of LC polyesters into an ordered state is effected upon melting. The possibility of preparing diverse polymeric articles by processing from a melt of these thermotropic polymers (self-reinforcing constructional plastics, coatings for optical cables, binders, fibres, or films) with high-strength characteristics has brought about the appearance in the scientific and patent literature of a large number of publications on the synthesis of LC polyesters and descriptions of their properties. The main part of these researches has been generalized in monographs, for example [1], and in review articles [2, 3]. However, as yet there is no review of the literature of recent years, especially devoted to problems in the synthesis of fibre-forming LC polyesters and the preparation of fibres based on them.

SYNTHESIS OF LC POLYESTERS

At present, a huge number of fibre-forming thermotropic polyesters has been synthesized, but only a few basic types have received industrial development. These are used also for the manufacture of fibres. In Table 1, we show basic types of commercial LC polyesters, whose chemical structure has been indicated only tentatively. It is known, for example, that about 20 forms of Xydar are produced, and the assortment of Vectra is still more diverse: it is reckoned to be above 75 types. It is not excluded that the differences between them are caused not only by different proportions of the elementary units in the molecules

---