5.4 Properties and Applications of Cellulose Triacetate Film

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Summary: The CTA film can be characterized by *e.g.* its relatively high moisture regain, significantly low birefringence, and moderate mechanical strength. Having been commercialized more than fifty years ago, it has been widely used as photographic film, protective film for polarizing plate, and optical compensation film for liquid crystal display (LCD). The photographic film application exploits the optical isotropy and unique physical properties of the CTA film. In the application of the CTA film to protective film for polarizing plate, its low in-plane birefringence is of particular importance. In the optical compensation to enhance the viewing angle of LCD, the CTA film, because of its moderate retardation in thickness direction (Rth), serves as an element of compensator as well as a base film. Considering the growth of the LCD market, the demand for CTA film is believed to be further expanding.

Keywords: cellulose triacetate (CTA), film, LCD, photographic film, polarizing plate, optical compensation, discotic liquid crystal, birefringence, retardation, hybrid alignment, TN, TFT, STN, polarized light

[a] Mr. Masahiko Murayama suddenly passed away on January 1st, 2004 and this article is his posthumous manuscript. We, the authors of this book, would like to express our sincere condolences

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1. Introduction

More than fifty years ago for the first time was commercialized the film of cellulose triacetate (CTA) for photographic application.

Featuring low flammability, the emergence of photographic film of CTA was striking since no film other than that of cellulose nitrate, which has the flammability problem, could have compromised mechanical and optical properties at that time. Later on, having been introduced to the animation, electric insulation, and masking applications, the number of applications of CTA film increased. However, after the emergence of films of synthetic polymers such as polyethyleneterephthalate (PET), the CTA film had no more been widely used because of its high price and insufficient mechanical strength *vis-à-vis* that of synthetic polymers. The only large market where the CTA film could survive was the photographic film application requiring the "easy-cut property" as one of the critical performances. The CTA film can even be torn easily by bear hands unlike synthetic polymer films; this property of the CTA film is of particular importance in the photographic film application as described later in this article.

Since the CTA film is excellently inert towards polarized light, it has been exclusively used as protective films for polarizing plate. The production amount of polarizing plate has increased in recent years as the liquid crystal display (LCD) technology, which requires one or more polarizing plates as an indispensable element, has prevailed in the market of flat panel displays. Furthermore, the market of CTA film coated with optically anisotropic layer such as Wide View Film™ of Fuji Photo Film is growing as it is verified that an optical compensation film with controlled birefringence is extremely effective to enhance the viewing angle of LCD and/or to prevent the undesirable retardation color of LCD. Expecting further growth of the LCD market, the future of CTA film is believed to be promissing.

CTA molecule is bulky and rigid. It easily forms microcrystallites. CTA is a unique polymer; it changes its physical properties depending on the crystallinity and orientation. Presumably owing to the acetyl carbonyl groups almost perpendicular to the polymer backbone, the birefringence of CTA is significantly small even when oriented. In this article, the structural and physical features of CTA polymer are described first. The explanation for the applications of CTA to photographic film, protective film for polarizing plate, and optical compensation film for LCD is followed. Finally, the perspective of the CTA film for the future is discussed.

2. Structure and Physical Properties of CTA

2-1 Molecular Structure

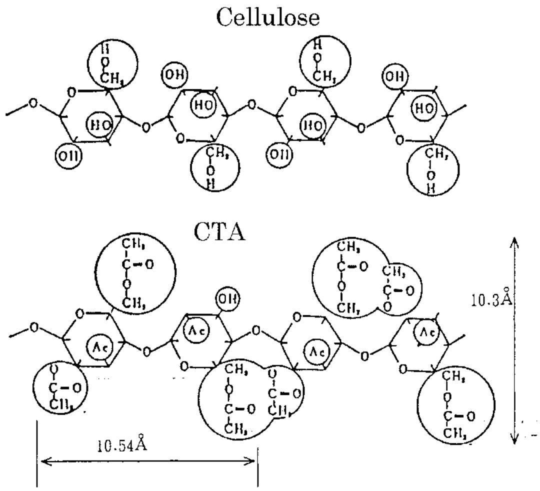


Fig. 1. Strucrures of cellulose and CTA.

The chemical structure of cellulose and that of CTA are shown in Figure 1 [1]. It is expected from the existence of bulky acetyl groups that CTA have a larger intermolecular free volume than cellulose. In fact, CTA shows relatively high moisture regain compared to synthetic polymers.

The essential requirements for a base film of photographic materials are (1) transparency, (2) surface smoothness, (3) sufficient mechanical properties (tensile strength, elastic modulus, tear strength), (4) anti-curl property, (5) dimensional stability towards temperature and humidity variations, (6) chemical stability (inertness towards photochemical layer), (7) antiflammability and the likes.

The anti-curl property as one of the most important requirements should be elaborate on here. In general, polymer films memorize a curled shape when stored in a form of roll at a relatively high temperature. In particular, a film material with a low glass transition temperature (T_g) is prone to memorize a curled shape: the tendency extremely deteriorates the quality of photographs at the processes of development and printing. It is generally difficult to cancel the memorized curl. Fortunately, owing to its moderate moisture absorbency, CTA possesses a unique character; it recovers the flatness and surface smoothness from the curl at the process of development. This tendency is shown in Figure 2, in comparison with PET, as ANSI curl value and moisture content as functions of swelling time in water [2].

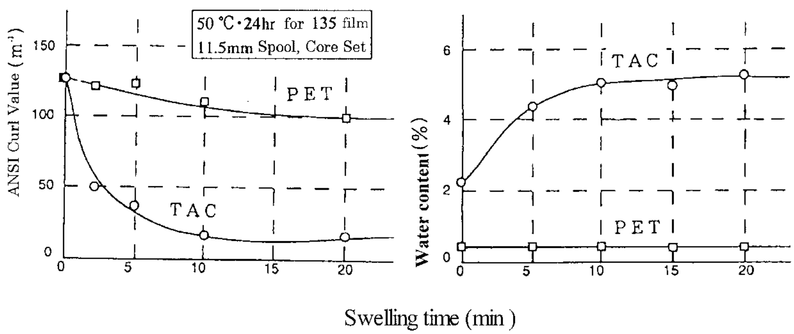


Fig. 2. Comparison of CTA with PET in the recovery of curl in water at 38℃.

2-2 Birefringence

Presumably because the acetyl carbonyl groups are almost perpendicular to the polymer backbone, CTA exhibits an only low in-plane birefringence even when the polymer is oriented. The typical CTA film shows a birefringence as low as at the order of ten to the power of minus five. The low birefringence of CTA is the main reason why it can be applied to optically isotropic films such as FUJI TAC^{TM} (protective film for polarizing plate).

2-3 Crystallinity

Although the CTA film was thought to be amorphous, an X ray diffraction study revealed that there exists a diffraction peak of (110) plane corresponding to a crystallinity of 25 - 30%. The diffraction peak is not sharp; judging by the Scherrer's theory, the crystallite consists of only 10 – 20 molecules. However, these micro crystallites act as junction points of polymer network, influencing the mechanical properties to a significant degree.

2-4 Thermal Properties

A DSC study of CTA film including plasticizers allows us to observe the T_g and the melting temperature (T_m). The T_g is observed at around 120 ° C. The T_m is not apparent enough. Upon heating, the thermal degradation occurs before the melting. This is the main reason why a film cannot be obtained from CTA by a melting process.

2-5 Film Preparation and Orientation

Figure 3 represents a typical machine to produce a film from CTA, where the polymer is dissolved in a mixed solvent mainly consisting of dichloromethane and cast from it. When certain shrinkage is not allowed on the metal band upon drying, the resulting stress leads to an orientation of film. Since the CTA molecule is rigid and bulky, it is not easy to be relaxed once oriented. The orientation influences the mechanical properties. For example, a film prepared by casting on mercury exhibits different mechanical properties compared to the conventional CTA film. This is because significant shrinkage is allowed by the fluidity of mercury upon drying, leaving a film with much less orientation.

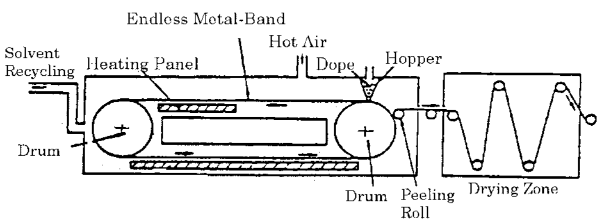


Fig. 3. Band casting machine.

2-6 Physical Properties

Table 1 summarizes the physical properties of typical transparent polymer films for photographic and other optical applications. The CTA film is superior in the curl recovery, high transparency, and low optical anisotropy. Its mechanical strength is at a level allowed to be used for the aforementioned applications. The superiority of CTA film is mainly due to its molecular characteristics. However, it should be also noted that the solvent cast technology and the high qualities such as the excellent flatness, which were refined over tens of years while the CTA film was used as a base film of photographic material, have contributed to the establishment of the superiority to other polymer films.

Table 1. Properties of optical-use films

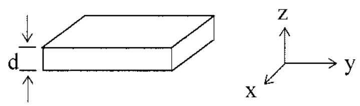
Material*	Transmit-tancy(%)	Haze (%)	Retardation (nm) Re	Rth	Refractive index	Remark
CTA	93	0.2	8	45	1.48	
A-PET	87	1.6	-0.6	96	1.58	
O-PET	89	-	-	>50	1.63	
PETG	90	0.5	-	-	-	
ARTON™	92	0.6	2	-	1.51	Brittle
ZEONEX™	91	0.3	1	-	1.53	Brittle
PMMA	93	0.3	1	-	1.49	Brittle

* PETG: copolyester of terephthalic acid with ethyleneglycol and 1,4-cyclohexanedimethanol. ARTON™ , ZEONEX™: both dicyclopentadiene- based polymer.

Retardation is genarally given by birefringence × film thickness. Re, in-plane retardation, and Rth, thickness retardation are defined as follows in the coordinate below. The d value is 80 m here.

Re: $(nx-ny) \times d$

Rth: $\{(nx+ny)/2 - nz\} \times d$



3. Application of CTA Film

3-1 Photographic Film

By making use of the characteristics described in the previous sections, the CTA film was used for various applications where a film should be stored in a form of roll. However, in the area of movie film and micro storage film, considering the mechanical durability upon projection and the chemical stability upon storage, the CTA film has been replaced with the PET film. In the category of photographic applications, the only (but largest) area remained for the CTA film is the color negative reversal film application, which is now one of the major applications of the material. Synthetic polymers such as PET have problems in (a) recovering from the curl in the development, (b) auto loading, (c) easy-cut property, and (d) splicing. These problems limit the application of synthetic polymers to a roll film product. Among these, the problem regarding the point (a) is already explained in section 2-1.

The point (b) is relevant to a jamming problem that arises when a significant curl is not removed. The PET film, which emerged in the market in the same era as the CTA film, is transparent and serves as a base film for photographic materials. However, since the PET film easily memorizes the curl shape when treated at a high temperature, it is generally used for films in a form of flat sheet (X-raying, G/A). The T_g of PET is at around 80 °C. The curl problem observed with PET can be resolved in the case of polyethylenenaphthalate (PEN) which has a high T_g at around 120 °C. In order to solve the problem of curling, it is to be annealed at a temperature below the Tg (A-PEN). The A-PEN film is commercialized recently for the APS new photographic system. In the new photographic system, the smaller film cartridge is supposed to accommodate as many photographs as forty. This means that the base film for the new system must be thinner than before. The demand for a thinner film led to the adoption, for the new system, of the A-PEN that has higher mechanical strength than the CTA film.

The point (c), easy-cut property, is seen as some kind of safeguard for the projection instruments in the event of jamming. The property also contributes to a better productivity in a cutting process for production of slides from film. The point (d) is relevant to the operability when cutting and pasting films to edit a movie. Since CTA is suitable for solvent-based adhesives, it is not easy to replace CTA with other synthetic materials as far as this type of application is concerned. Given that each material has *the pros and cons* as a base film when looking at individual application, the CTA film is believed to continue to be used in future in this area of photographic base film.

3-2 Protective Film for Polarizing Plate

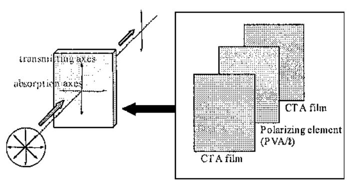


Fig. 4. Protective film for polarizing plate.

The polarizing element of polarizing plate consists of iodine or dyes absorbed onto polyvinylalcohol (PVA). The PVA is uniaxially oriented. A polarized light is generated by absorbing the light vibrating the same direction as the PVA is oriented. In order to prevent the oriented PVA from shrinking and to prevent the iodine or dyes from evaporation, a polarizing plate has a structure in which protective films sandwich the polarizing element (Figure 4). The protective film must have high transparency and low birefringence so that it does not perturb a polarized light. At the same time, it should have certain permeability for vaporized water so that the water from water-based adhesive used to pile up the polarizing element and the protective films is allowed to evaporate. It should also be inexpensive. The CTA film has been used for this application for long time since it meets all these requirements. Nowadays, the most major usage of polarizing plates is for LCDs of TVs, personal computers, and mobile phones. An LCD turns on and off the light when the direction of vibration of polarized light is changed by the orientation of liquid crystalline molecules. The orientation of liquid crystalline molecules changes in response to the voltage applied. In this system, a polarizing plate that is to isolate an linear polarized light from the natural unpolarized light is an indispensable element. For an LCD with the backlight system, two polarized plates are used; one of them is placed in front of the LCD cell and the other at the back. Therefore, four CTA films as protective film for polarizing plate are used in a LCD as such. The most essential requirements for protective film for polarizing plate for the LCD application are optical isotropy, less foreign particles, and flatness. Optical anisotropy of and foreign particles in the protective films placed between a polarizing element and the LCD cell lead to problems of retardation color of display, light leakage at the dark state, and bright dot error at the same state. This means that the LCD application requires higher quality than the photographic application. These stringent requirements are satisfied by Fuji Photo Film by means of the solvent casting technology that has been refined through the production of the high quality base films of CTA for the photographic application. As listed in Table 1, other materials have been developed for optical applications. Although those other materials have *the pros and cons*, they fall short of CTA on the whole. It is expected that the CTA film continue to be used in the further growing LCD market.

3-3 Optical Compensation Film for LCD

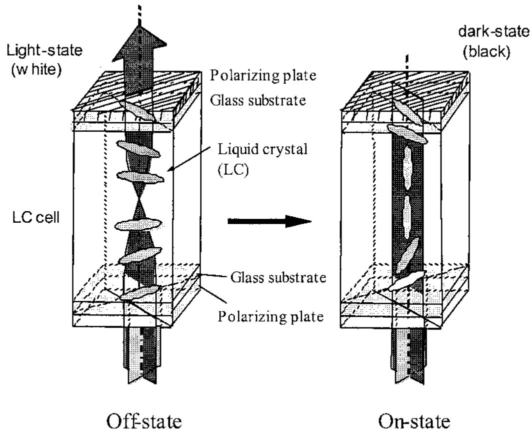


Fig. 5. The principle of TN(twisted nematic) mode TFT-LCD.

Currently, the most major method for color LCD is the TN-TFT. TN stands for Twisted-Nematic method as a type of liquid crystal cell. TFT stands for thin film transistor that realizes what is called as active-matrix method. The TN method makes use of optical rotation (the wave-guide effect) to switch the ON and OFF modes. The TN has become prevailing in the market of color LCDs since it has advantages over the Super Twisted-Nematic (STN), which utilizes birefringence for the switching, in terms of undesirable retardation color, suitability for wide screen, contrast, and response speed. (See refs. 3 – 8 for the details of principles of TN and other types of LCDs.) However, there is still room for improvement in the TN method; viewed from directions other than the normal one to the panel, black and white images are reversed and/or colors that are not supposed to be part of the image are observed. In order to overcome the problem, several means have been proposed. Fuji Photo Film recently developed "WV Film™" using the CTA film to improve the problem of narrow viewing angle of the TN LCD. By only inserting WV Film™ between the LCD cell and a polarizing plate, the quality of display image viewed from any angles of elevation or azimuth (the viewing angle dependence) is significantly improved. The response from the market has been very positive.

In the dark state, which requires the optical compensation, of the actual TN LCD, liquid crystalline molecules take a complicated orientation as shown in Figure 5. WV Film™ composes of the CTA film and an optical anisotropic layer of a couple of micrometer thickness in which discotic liquid crystals are aligned in a special manner to cancel the birefringence due to the complicated orientation of the rod-like molecules in TN-LCD. The special manner of alignment has been named as "hybrid alignment". In this set up, the CTA film possessing a negative birefringence plays the role to compensate the birefringence due to the rod-like liquid crystalline molecules that are aligned perpendicular to the panel.

As understood from the aforementioned principle of optical compensation, the best optical compensation is made when the absolute value of retardation with regard to the thickness direction of film for this purpose is almost equal to that of the LCD cell. Therefore, the retardation with regard to thickness direction (Rth) defined as the product of birefringence and film thickness is one of the most important factors contributing to the performance of optical compensation film. The CTA film is used for the application of optical compensation since it has an appropriate Rth value.

As a result from today's market growth and technical evolution, there is a great demand for reducing the thickness of LCD panel. Fuji Photo Film has developed a novel CTA film for the second generation of WV film that features a reduced thickness and more transmittance (Figure 6). The first generation of WV film is supposed to be placed on a polarizing plate by using an adhesive. This means that two CTA films, one for the protection purpose and the other for the optical compensation purpose, are supposed to be piled up. The novel CTA film possesses as twice Rth as the conventional one; this feature enables the novel CTA film to function as the optical compensation film and protective film at the same time. WV film is a fruit of the assets of Fuji Photo Film in the fields of optical engineering, film casting technology, and coating technology [8].

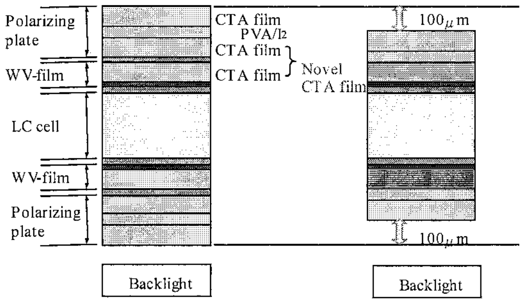


Fig. 6. Concept of the 2nd generation WV Film^{TM}. The left shows the 1st generation and the right, the 2nd generation WV Film^{TM}.

4. Perspective of CTA Film

CTA is from natural material, cellulose. It has been used since tens of years ago. Yet, it is environmentally friendly and meets the today's needs as such, considering the suitability for recycling for example. The CTA film has been widely used because of its superiorities in terms of optical and mechanical properties and low production cost. It is expected that the CTA film continue to be widely used based on the superiorities. In particular, in the growing market of LCD, the demand for CTA film is also believed to be further expanding. R & D activities should continue with a view to making further improvement and progress.

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