



MECHANICAL PROPERTIES OF PLASTICIZED CELLULOSE ESTER FILMS AT ROOM AND HIGH TEMPERATURES

Mohd Edeerozey Abd Manaf¹, Koh-Hei Nitta² and Masayuki Yamaguchi³

¹Carbon Research Technology Group, Faculty of Manufacturing Engineering, Universiti Teknikal Malaysia Melaka, Durian Tunggal, Melaka, Malaysia

²Graduate School of Natural Science and Technology, Kanazawa University, Kakuma Campus, Kanazawa, Japan

³School of Materials Science, Japan Advanced Institute of Science and Technology, Asahidai, Nomi, Ishikawa, Japan

E-Mail: edee@utem.edu.my

ABSTRACT

Cellulose ester is a biomass-derived material and exhibits excellent heat resistance and high transparency, properties required for optical film application. Recently, attention has been paid to cellulose esters due to their potential application as a functional film. Some cellulose esters such as cellulose acetate propionate (CAP) show extraordinary dispersion of orientation birefringence, in which the birefringence increases with increasing wavelength, a property required as a retardation film. The similar behaviour is also observed for cellulose triacetate (CTA) plasticized with tricresyl phosphate (TCP). In this study, the mechanical properties of pure and plasticized CAP and CTA at room and high temperatures are investigated to relate with their birefringence property. At room temperature, CTA film shows a higher brittleness than CAP film. At 15 K above their respective T_g , pure CAP and CTA can be stretched to draw ratio of 5.0 and 2.0, respectively. However, the addition of TCP slightly decreases the stretchability in both CAP and CTA to draw ratio of 4.5 and 1.5, respectively. The stretchability of both pure and plasticized CAP and CTA is found to increase with the increase of stretching temperature, which is useful to increase the value of orientation birefringence as it increases with draw ratio. However, birefringence value becomes lower at higher temperature. Thus, to obtain an optimum value of orientation birefringence, a balance between the draw ratio and stretching temperature has to be considered.

Keywords: cellulose ester, mechanical properties, optical film.

INTRODUCTION

Cellulose-based polymers can decompose naturally and when incinerated, releases relatively less toxic substance. These properties of cellulose fulfill the current need for environmentally friendly biomass-based materials. Traditionally, some cellulose esters such as cellulose triacetate (CTA) have been utilized as photographic and polarizer protective films due to their excellent heat resistance and high transparency (Sata *et al.* 2004), (Edgar *et al.* 2001). Recently, attention has been paid to cellulose esters for their optical property, with a potential application as a functional film. Certain cellulose esters such as cellulose acetate propionate (CAP) and cellulose acetate butyrate (CAB) are found to show extraordinary dispersion of orientation birefringence, in which the birefringence increases with increasing wavelength, a property required as a retardation film (Tagaya *et al.* 2001), (Uchiyama and Yatabe, 2003). Furthermore, addition of plasticizer is found to be effective in modifying the orientation birefringence in cellulose esters (Abd Manaf *et al.* 2011a), (Abd Manaf *et al.* 2013).

Cellulose triacetate (CTA) is a type of cellulose esters, with more than 92 percent of the hydroxyl group is acetylated (Namazi and Jafari Rad, 2004). Hot-drawn CTA films show negative orientation birefringence that decreases with increasing wavelength. Addition of a small amount of certain plasticizer such as tricresyl phosphate (TCP), is reported to change the orientation birefringence of CTA from negative to positive birefringence (Abd Manaf *et al.* 2011). Furthermore, the wavelength

dependence of birefringence becomes the so-called extraordinary wavelength dispersion of birefringence i.e., magnitude of birefringence increases with increasing wavelength, a property required for retardation films (Yamaguchi and Masuzawa, 2007), (Kuboyama *et al.* 2007).

Cellulose acetate propionate (CAP) is a mixed cellulose ester that contains propionyl group, in addition to acetyl group (Figure-1). Unlike commonly used optical polymers such as polycarbonate (PC) and polymethyl methacrylate (PMMA), CAP films show extraordinary wavelength dispersion of birefringence upon hot-drawing. The reason of this is due to combination between negative birefringence with strong wavelength dispersion originated from the acetyl group and positive birefringence with weak wavelength dispersion originated from the propionyl groups. The addition of plasticizer such as TCP further increases the magnitude of the orientation birefringence of CAP while maintaining the wavelength dispersion (Abd Manaf *et al.* 2011).

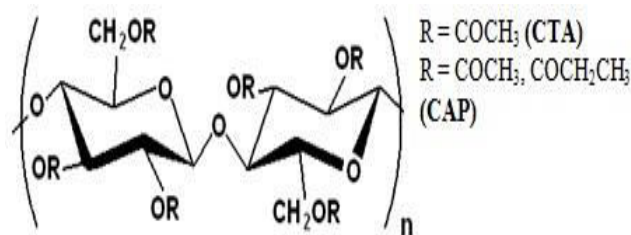


Figure-1. Molecular structures of cellulose esters.



The objective of this research is to evaluate the mechanical properties of pure and plasticized CAP and CTA at room and high temperatures. This is because generally optical films used in various applications produced by uniaxial or biaxial stretching at high temperatures. For that reason, information on the temperature dependence of the mechanical properties of pure and plasticized CTA and CAP films at high temperatures is important in designing the process to produce reliable optical films with required properties

EXPERIMENTAL

Materials

The polymeric materials used in this study were commercially available cellulose esters such as cellulose acetate propionate (CAP) and cellulose triacetate (CTA). CAP employed in this study was produced by Eastman Chemical, while CTA was produced by Acros Organics. The molecular characteristics are summarized in Table-1. The plasticizer used in this study was tricresyl phosphate (TCP) produced by Daihachi Chemical Industry.

Table-1. Characteristics of CTA and CAP.

Sample	Compositions, wt%			Molecular weights	
	acetyl	propionyl	hydroxyl	Mn (x105)	Mw (x105)
CTA	43.6 (2.96) *	-	0.9	1.3	3.5
CAP	2.5 (0.19) *	46 (2.58)*	1.8	0.77	2.1

Sample Preparation and Testing

Pure and plasticized CTA and CAP films were prepared using a solution cast method since melt processing is not applicable for CTA due to its severe thermal degradation (Ohkita *et al.* 2004). Both cellulose esters are plasticized using 10 wt% of tricresyl phosphate (TCP). Cellulose ester in powder form were dissolved into chloroform with TCP plasticizer and stirred for 24-hours at room temperature to get a uniformly mixed solution. The solution was cast onto a metal plate and left at room temperature for 48-hours to allow the solvent to evaporate slowly in order to obtain a smooth and thin film. The obtained films of CAP/TCP and CTA/TCP are optically transparent as in their pure films, while the thickness ranges from 150 to 200 μm . They were subsequently kept in a humidity chamber (Yamato, IG420) at 25 °C and 50 %RH at least for a day as cellulose ester films are highly sensitive to moisture (Abd Manaf *et al.* 2011b).

Tensile tests on pure and plasticized films of CTA and CAP were performed using a tensile testing machine (Instron-4466) at room (controlled at 25 °C) and high temperatures, i.e., glass transition temperature T_g , 5 K

below T_g and 15 K above T_g . T_g is defined as the peak of the loss modulus E'' measured earlier using dynamic mechanical analysis (DMA). The high stretching temperatures applied for each material are shown in Table-2. Samples were drawn at a constant elongation rate of 30 mm/min. Dumbbell-shaped specimens having a gauge length of 10 mm and a width of 4 mm were used. The stress-strain data generated during the stretching were recorded for further analysis.

Table-2. Stretching temperatures for pure and plasticized films of CAP and CTA.

Composition	$T_g - 5 \text{ K}$ (°C)	T_g (°C)	$T_g + 15 \text{ K}$ (°C)
CAP(100)	142	147	162
CAP/TCP (90/10)	110	115	130
CTA (100)	177	182	197
CTA/TCP (90/10)	155	160	175

The birefringence values of the drawn films were measured by an optical birefringence analyzer (Oji Scientific Instruments, KOBRA-WPR) at room temperature. The measurements were performed as a function of the wavelength between 450 and 800 nm by changing the color filters.

EXPERIMENTAL RESULTS

Tensile Properties at the Room Temperature

The stress-strain curves for pure and plasticized CAP and CTA at room temperature are shown in Figure-2 and Figure-3, respectively. From Figure-2, CTA shows a much higher tensile strength but lower elongation compared to pure CAP, indicating the brittle behavior of CTA film at room temperature. The higher tensile strength in CTA is attributed to the high storage modulus E' of CTA at room temperature as determined by the dynamic mechanical analysis (Abd Manaf *et al.* 2011a). Addition of 10 wt% TCP, however, does not seem to significantly change the stress-strain behavior of the CTA. On the other hand, CAP shows the characteristic of a ductile polymer, with relatively low strength and large elongation as demonstrated in Figure-3. The relatively low tensile strength is understandable as CAP shows a lower storage modulus E' than CTA at room temperature. Addition of TCP seems to lower the strain hardening effect in CAP as demonstrated by a flat stress curve in the plasticized CAP for the strain range above the yield point. Both CAP and CTA show a decrease in toughness, ultimate strength and elongation at break with the TCP addition.

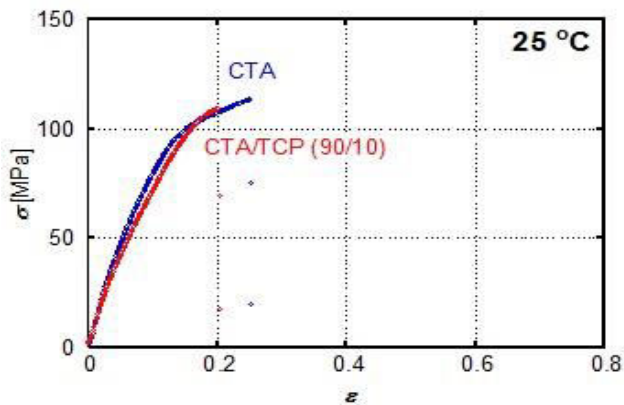


Figure-2. Stress-strain curves for pure and plasticized CTA at room temperature.

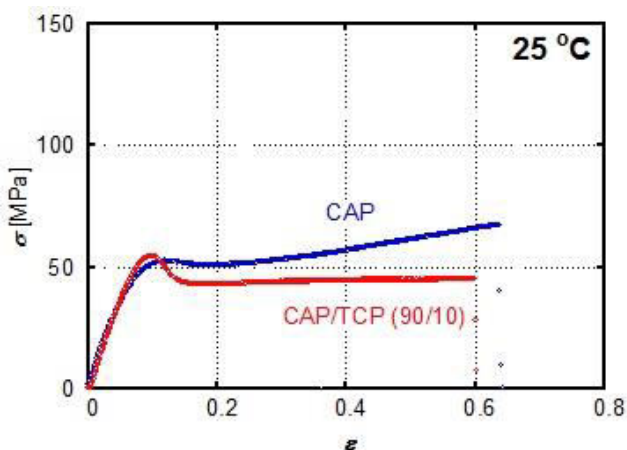


Figure-3. Stress-strain curves for pure and plasticized CAP at room temperature.

Tensile Properties of CAP and CAP/TCP Blend at High Temperatures

For both CAP and CAP/TCP (90/10), the Young's modulus and ultimate tensile strength decrease while the elongation increases with the increase of stretching temperature as shown in Figure-4 and Figure-5. As the stretching temperature is raised, the CAP and CAP/TCP films become more ductile. At the stretching temperature of $T_g + 15$ K, both pure and plasticized CAP show no yield point, which is a characteristic generally shown by elastomeric polymers. Furthermore, as shown in Figure-4, CAP film stretched at high temperature consistently shows the strain hardening behavior, similar to what observed when it is stretched at room temperature. This is due to the fact that at high deformation, polymer chains are highly oriented and aligned, thus contributes to strain hardening. From Figure-5, the plasticized CAP/TCP (90/10) films show a weak strain hardening behavior which further weakens with the increase of stretching temperature. The result indicates that the aligned chains in pure CAP are stiffer than that of plasticized CAP. The stretchability of CAP and CAP/TCP (90/10) increases almost seven and six-folds respectively, when the stretching temperature is increased from room temperature

to $T_g + 15$ K. At 15 K above their respective T_g , CAP can be stretched over draw ratio of 5.0 (strain = 4.0), while the CAP/TCP (90/10) is able to withstand a draw ratio of 4.5 without rupture.

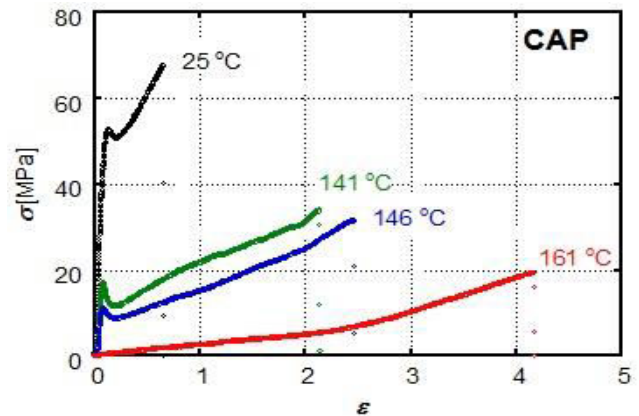


Figure-4. Stress-strain curves for pure CAP at room temperature, $T_g - 5$ K, T_g and $T_g + 15$ K.

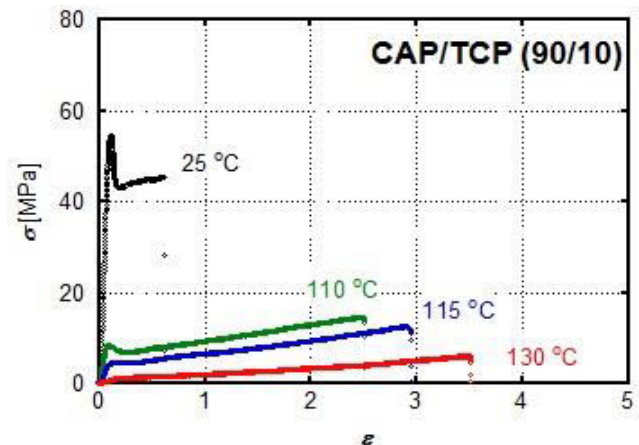


Figure-5. Stress-strain curves for plasticized CAP at room temperature, $T_g - 5$ K, T_g and $T_g + 15$ K.

Tensile Properties of CTA and CTA/TCP Blend at High Temperatures

For CTA and CTA/TCP films, Young's modulus and ultimate tensile strength decrease, while elongation increases with the increase of the stretching temperature as shown in Figure-6 for pure CTA and Figure-7 for plasticized CTA. The results are similar to what observed in the CAP/TCP system. At higher temperatures, both CTA and CTA/TCP (90/10) show a more ductile behavior. However, contrary to the CAP/TCP system, CTA and CTA/TCP (90/10) do not become completely elastomeric, even at the $T_g + 15$ K. This explains the overall low degree of the stretchability in the CTA/TCP system compared to the CAP/TCP system. From the elongation results, it can be estimated that at $T_g + 15$ K, CTA can be stretched up to a draw ratio of nearly 2.0, while CTA/TCP (90/10) can be stretched up to a draw ratio of only 1.5.

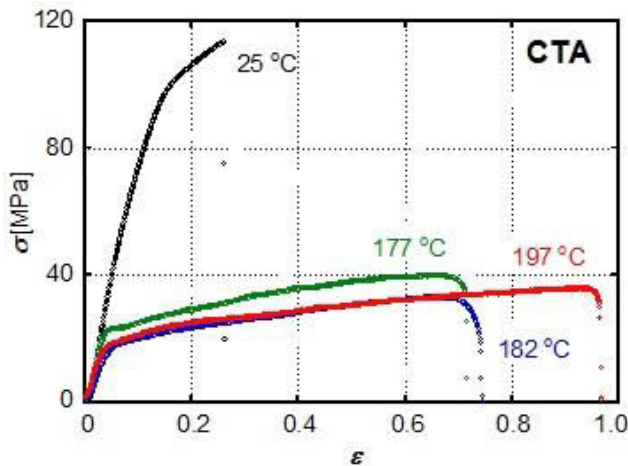


Figure-6. Stress-strain curves for pure CTA at room temperature, $T_g - 5$ K, T_g and $T_g + 15$ K.

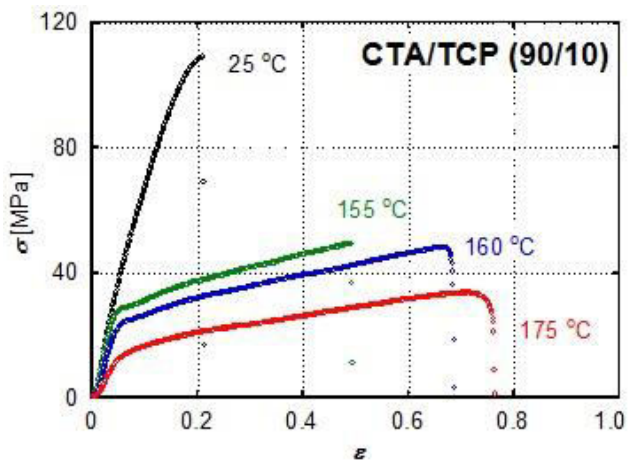


Figure-7. Stress-strain curves for plasticized CTA at room temperature, $T_g - 5$ K, T_g and $T_g + 15$ K.

Stretching Conditions and Orientation Birefringence

The relation of stretching condition and orientation birefringence is discussed in this section. As discussed above, the stretchability of films decreases, while the stress generated increases with decreasing stretching temperature. Figure-8 shows the wavelength dependence of orientation birefringence, Δn of pure CAP stretched at various temperatures. As shown here, CAP shows extraordinary wavelength dispersion of birefringence – a property required as retardation films (Yamaguchi *et al.* 2007), (Kuboyama *et al.* 2007). It is also found that orientation birefringence increases with decreasing stretching temperature.

As stress is higher at low temperature ranges, the result indicates that the value of orientation birefringence increases with the increase of stress generated. This is in agreement with the stress-optical rule for rubber and melting polymer (Treloar, 1975), although the mechanisms involved in the determination of orientation birefringence in cellulose esters does not strictly follow the stress optical law as has been discussed in details in

our previous papers (Abd Manaf *et al.* 2011a), (Yamaguchi *et al.* 2009).

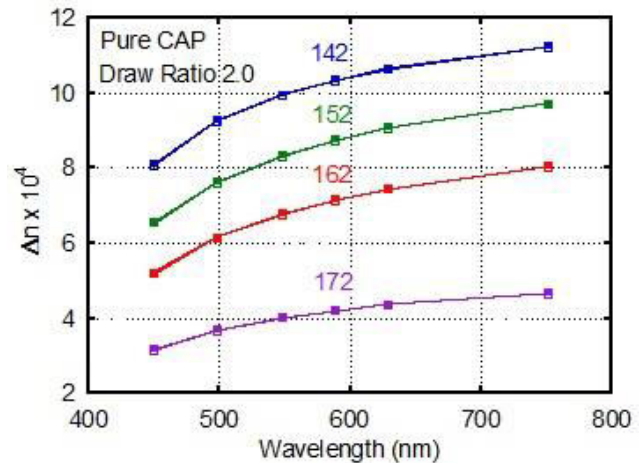


Figure-8. Effects of stretching temperature on orientation birefringence, Δn of CAP.

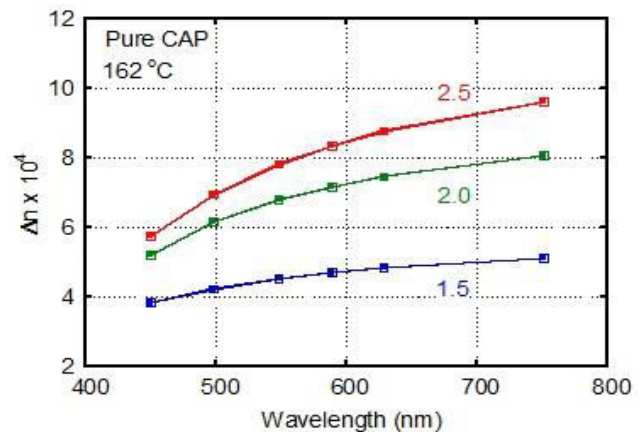


Figure-9. Effects of draw ratio on orientation birefringence, Δn of CAP.

The wavelength dependence of orientation birefringence, Δn of pure CAP stretched at various draw ratios is shown in Figure-9. As seen here, orientation birefringence increases with increasing draw ratio. From the viewpoint of stretching temperature, a decrease in stretching temperature increases the orientation birefringence, but at the same time decrease the degree of stretchability, i.e. draw ratio – which in turn decreases the orientation birefringence. Birefringence Δn is inversely proportional to film thickness, d as shown in the following equation:

$$\Delta n = \Gamma / d \quad (1)$$

where Γ is retardation. In other words, a balance between the draw ratio and stretching temperature has to be considered in order to obtain an optimum value of orientation birefringence, as film thickness can be reduced by increasing the birefringence value.



CONCLUSIONS

Films of pure and plasticized CAP and CTA were stretched at four different temperatures – room, $T_g - 5$ K, T_g , and $T_g + 15$ K and the tensile properties were analyzed. At room temperature, CTA film shows a higher brittleness than CAP film which possibly due to the existence of crystallites. While addition of TCP decreases the T_g for both CAP and CTA (Abd Manaf *et al.* 2011a), the mechanical behavior of plasticized CAP differs to that of CTA in regard to their pure forms. Plasticized CAP shows reduced brittleness than pure CAP, while there was no significant reduction in brittleness in the plasticized CTA compared to the pure CTA, when drawn at their respective T_g . Elongation at break, which indicates the stretchability shows a slight decrease in both CTA and CAP with the addition of TCP. Increase in stretching temperature increases the stretchability of all films – pure and plasticized CAP and CTA. Contrarily, it decreases both Young's modulus and ultimate tensile strength – both properties associated to the amount of generated stress in the films. Orientation birefringence is known to increase with decreasing temperature and increasing draw ratio (Yamaguchi *et al.* 2009). The results in this study show that draw ratio can be increased by increasing the stretching temperature, which in return decrease the values of birefringence. Thus, in order to obtain an optimum value of orientation birefringence, a balance between the draw ratio and stretching temperature has to be considered.

REFERENCES

- [1] Abd Manaf, M. E., Tsuji, M., Shiroyama, Y. and Yamaguchi, M. (2011). Wavelength dispersion of orientation birefringence for cellulose esters containing tricresyl phosphate. *Macromolecules*, 44(10), pp. 3942-3949.
- [2] Abd Manaf, M. E., Tsuji, M., Nobukawa, S. and Yamaguchi, M. (2011). Effect of moisture on the orientation birefringence of cellulose esters. *Polymers*, 3(2), pp. 955-966.
- [3] Abd Manaf, M. E., Miyagawa, A., Nobukawa, S., Aoki, Y. and Yamaguchi, M. (2013). Incorporation of low-mass compound to alter the orientation birefringence in cellulose acetate propionate. *Optical Materials*, 35(7), pp. 1443-1448.
- [4] Edgar, K. J., Buchanan, C. M., Debenham, J. S., Rundquist, P. A., Seiler, B. D., Shelton, M. C. and Tindall, D. (2001). Advances in cellulose ester performance and application. *Progress in Polymer Science*, 26(9), pp. 1605-1688.
- [5] Kuboyama, K., Kuroda, T. and Ougizawa, T. (2007). Control of wavelength dispersion of birefringence by miscible polymer blends. In *Macromolecular Symposia* (Vol. 249, No. 1, pp. 641-646). WILEY-VCH Verlag.
- [6] Namazi, H. and Jafari Rad, S. (2004). Synthesis of block and grafted copolymers containing spacer-linked chromophore based on cellulose and polyethylene glycol. *Journal of applied polymer science*, 94(3), pp. 1175-1185.
- [7] Ohkita, H., Tagaya, A. and Koike, Y. (2004). Preparation of a zero-birefringence polymer doped with a birefringent crystal and analysis of its characteristics. *Macromolecules*, 37(22), pp. 8342-8348.
- [8] Sata, H., Murayama, M. and Shimamoto, S. (2004). Properties and applications of cellulose triacetate film. In *Macromolecular Symposia* (Vol. 208, No. 1, pp. 323-334). WILEY-VCH Verlag.
- [9] Tagaya, A., Iwata, S., Kawanami, E., Tsukahara, H. and Koike, Y. (2001). Anisotropic molecule dopant method for synthesizing a zero-birefringence polymer. *Japanese Journal of Applied Physics*, 40(10R), pp. 6117-6123.
- [10] Treloar, L. R. G. (1975). *The physics of rubber elasticity*. Oxford University Press.
- [11] Uchiyama, A. and Yatabe, T. (2003). Control of wavelength dispersion of birefringence for oriented copolycarbonate films containing positive and negative birefringent units. *Japanese Journal of Applied Physics*, 42(11R), pp. 6941-6945.
- [12] Yamaguchi, M. and Masuzawa, K. (2007). Birefringence control for binary blends of cellulose acetate propionate and poly (vinyl acetate). *European polymer journal*, 43(8), pp. 3277-3282.
- [13] Yamaguchi, M., Okada, K., Manaf, M. E. A., Shiroyama, Y., Iwasaki, T. and Okamoto, K. (2009). Extraordinary wavelength dispersion of orientation birefringence for cellulose esters. *Macromolecules*, 42(22), pp. 9034-9040.