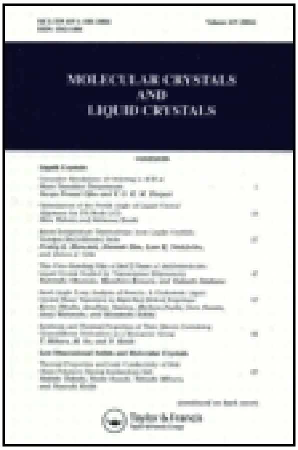


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Effect of Plasticization on Physical and Optical Properties of Triacetyl Cellulose Films for LCD Application

Hyeong Tae Kim [a b], Myeong Hee Kim [a c], Bori Kim [a d], Chong Min Koo [a], Khee Kahb Koo [b] & Soon Man Hong [a]

[a] Hybrid Materials Research Center, Korea Institute of Science and Technology, Hawolgok-dong, Sengbuk-gu, Seoul, Korea

[b] Department of Chemical and Biological Engineering, Sogang University, Sinsu-dong, Mapo-gu, Seoul, Korea

[c] Department of fiber and polymer Engineering, Hanyang University, Haengdang-dong, Seongdong-gu, Seoul, Korea

[d] Department of Chemistry, Kyung Hee University, Hoegi-dong, Dongdaemun-gu, Seoul, Korea

Version of record first published: 05 Oct 2009

To cite this article: Hyeong Tae Kim, Myeong Hee Kim, Bori Kim, Chong Min Koo, Khee Kahb Koo & Soon Man Hong (2009): Effect of Plasticization on Physical and Optical Properties of Triacetyl Cellulose Films for LCD Application, Molecular Crystals and Liquid Crystals, 512:1, 188/[2034]-198/[2044]

To link to this article: http://dx.doi.org/10.1080/15421400903050905

Mol. Cryst. Liq. Cryst., Vol. 512, pp. 188/[2034]–198/[2044], 2009

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400903050905

Effect of Plasticization on Physical and Optical Properties of Triacetyl Cellulose Films for LCD Application

Hyeong Tae Kim[1,2], Myeong Hee Kim[1,3], Bori Kim[1,4], Chong Min Koo[1], Khee Kahb Koo[2], and Soon Man Hong[1]
[1]Hybrid Materials Research Center, Korea Institute of Science and Technology, Hawolgok-dong, Sengbuk-gu, Seoul, Korea
[2]Department of Chemical and Biological Engineering, Sogang University, Sinsu-dong, Mapo-gu, Seoul, Korea
[3]Department of fiber and polymer Engineering, Hanyang University, Haengdang-dong, Seongdong-gu, Seoul, Korea
[4]Department of Chemistry, Kyung Hee University, Hoegi-dong, Dongdaemun-gu, Seoul, Korea

Mechanical properties, thermal stability and optical properties of triacetyl cellulose (TAC) films plasticized by three types of plasticizer, triphenyl phosphate (TPP), biphenyldiphenyl phosphate (BDP) and a mixture of TPP and BDP have been investigated in order to find the optimum plasticization condition for a protective film application in LCD. Mechanical properties such as modulus, tensile strength and elongation at break, and thermal property were significantly distinguished according to the type of plasticizer. TPP worked as the most effective plasticizer for TAC in the viewpoint of the mechanical properties. TAC/TPP showed the largest increase in elongation at break and the biggest reduction in the glass transition temperature at the same plasticizer level. However, TPP had the worst thermal stability. A mixture of TPP and BDP achieved the compromising plasticization to produce the moderate mechanical properties and thermal stability of TAC films for protective film application in LCD.

Keywords: LCD; plasticizer; protective film; triacetyl cellulose; triphenyl phosphate

This work was financially supported by a grant from the Materials and Components Industry Program funded by the Ministry of Knowledge Economy, Republic of Korea and partially by a grant from Hybrid Materials Research Center of Korea Institute of Science and Technology (KIST).

Address correspondence to Soon Man Hong, Polymer Hybrids Research Center, Korea Institute of Science and Technology, 39-1 Hawolgok, Seongbuk, Seoul 136-791, Korea. E-mail: smhong@kist.re.kr

INTRODUCTION

Triacetyl cellulose (TAC) is one of the most common cellulose derivatives in the fiber and textile industries, optical film for a polarizer application in liquid crystal display (LCD) and cigarette filter tow and is usually manufactured from cotton linters or high quality wood dissolving pulps. It has been exclusively used as a protective film for polarizing plate in LCD thanks to its high transparence, optical isotropy, moderate mechanical properties, and good thermal stability [1–4].

The most essential requirement for the protective film is optical transmittance and optical isotropy, because optical anisotropy of the protective film can make problems of retardation color of display, and light leakage and bright dot error at the dark state. In addition, TAC protective film has to prevent the uniaxially oriented PVA from shrinking and to prevent the iodine or dyes from evaporation, so that it needs moderate mechanical properties, and thermal and dimensional stability [1,2].

TAC is a quite stiff resin because of its high glass transition temperature around 200°C. So, it should be plasticized to meet the requirement for the protective film application. Physical and mechanical properties of TAC films are highly dependent of contents and types of plasticizer [2,5]. However, few academic researches have been reported because most studies on the TAC film have been carried out by industry demand.

Phosphate derivatives such as triphenyl phosphate (TPP) are the good candidate plasticizer for optical TAC film. Because they are ecologically friendly plasticizers and they can works as a flame retardant at the same time. During thermal degradation, TPP generates pyro phosphoric acid, which plays as heat transfer barrier [6].

In this study, mechanical properties, thermal stability and optical properties of TAC films plasticized by three types of phosphate systems, triphenyl phosphate (TPP), biphenyldiphenyl phosphate (BDP) and a mixture of TPP and BDP have been investigated not only in order to understand the effect of the plasticizer, but also to find the optimum plasticization condition for LCD applications.

EXPERIMENTAL

Materials

Neat TAC flake with $Mw = 281{,}000\,g/mol$ and $Mw/Mn = 3.9$ was obtained from Eastman Kodak. Methylene chloride (99.99%) and methanol (99.99%) used as a solvent were purchased from Sigma

Aldrich. Triphenyl phosphate (TPP) and biphenyldiphenyl phosphate (BDP) used as a plasticizer were purchased from Sigma Aldrich and Hyosung Chemicals, respectively.

Film Preparation

TAC flakes and plasticizers were dissolved in a mixed solvent of methylene chloride and methanol in 9 to 1 ratio. The TAC solution was filtered with a mesh SUS filter in order to remove impurities and aged for 2 days before casting, The TAC dope solution was cast on the glass using a bar coater and then dried via three steps; in first 2 hour drying at the room temperature and then 20 minute drying at 80°C, and finally 1hour drying at 110°C. The prepared TAC films contained less than 1% of residual solvent. Average film thickness was about 80 μm.

Characterization

Uniaxial extension test was performed from universal testing machine (UTM, H5KT) with ASTM D-882. Sample dimensions were guage length of 25 mm, width of 5 mm, and thickness of 80 μm. Extension rate was 10 mm/min. Storage modulus and tan δ were measured by dynamic mechanical analyzer (DMA Q-800, TA instruments) under nitrogen at the heating speed of 10°C/min. Thermalgravimetry analysis was performed by TA instrument TGA 2950 under nitrogen with a heating rate of 20°C/min. Optical transmittance was measured by UV spectrophotometer (HP HEWLETT PACKARD 8453). Optical isotropy represented by in-plane retardation, Re and out of plane retardation, Rth was measured by Retardation Inspection System, RETS-100 Otsuka Electronics.

RESULTS

Figure 1 shows representative stress–strain curves of neat TAC and the plasticized TAC films. Neat TAC film showed steep and linear increase in tensile stress until yield point appeared at the small strain of about 5% and then slow increase up to the break point around 30%. Tensile strength was about 155 MPa. The plasticized TAC film also showed the same patterns as the neat one. However, yield stress, yield strain and tensile strength were linearly decreased with the contents of plasticizer while extension gradually increased with the plasticizer, making for a tougher film.

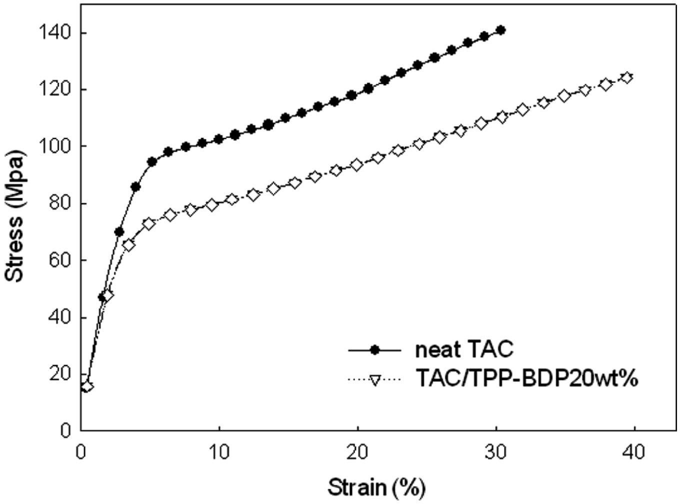
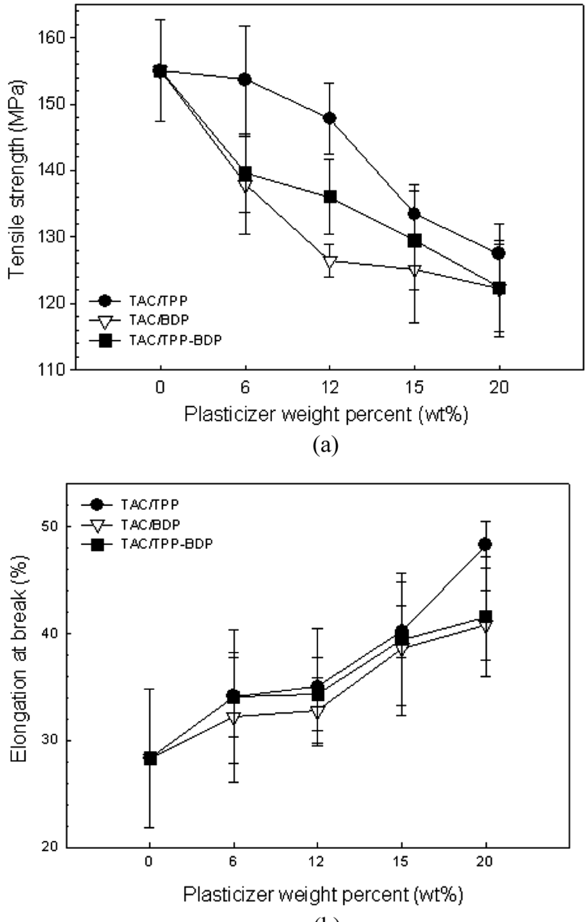


FIGURE 1 Typical stress-strain curves for neat TAC (–●–) and the plasticized TAC films (–▽–).

Figure 2 shows the tensile strength and elongation at break of TAC films obtained by uniaxial extension tests. Three types of plasticizers, TPP, BDP and a mixture of TPP and BDP were used as a plasticizer and plasticizer level was ranging from 6 to 20 wt%. Each film was uniaxially drawn to machine direction (MD) as well as transverse direction (TD). MD direction corresponds to the moving direction of bar coater. Tensile properties rarely depended on the drawing direction. Tensile strength and elongation at break depended not only on plasticizer contents, but also types of plasticizer. As the plasticizer contents increased, tensile strength decreased but elongation at break increased. TAC film plasticized by TPP had largest tensile stress and elongation at break. In contrast, TAC film with BDP plasticizer showed smallest ones. The film with a mixture of TPP and BDP was in between TAC/TPP and TAC/BDP. The tensile properties were summarized in Table 1.

Figure 3 shows storage modulus and tan δ of TAC/TPP-BDP films with various plasticizer contents. Storage modulus (E′) represents the stored elastic energy and tan $\delta = E''/E'$ is closer to the dissipation of energy. Storage modulus gradually decreased with the temperature until a steep drop appeared at the glass transition. Glass transition temperature, Tg was determined by the maximum point of tan δ. As the plasticizer level increased, storage modulus increased and Tg



(a)

(b)

FIGURE 2 (a) Tensile strength and (b) elongation at break of neat TPP(–●–), TAC/BDP (–▽–), TAC/TPP-BDP (–■–) films with various plasticizer contents.

decreased. Neat TAC had Tg at 207°C. TAC/TPP and TAC/BDP films showed the same plasticizer dependency on the properties.

Figure 4 shows storage modulus and tan δ of TAC films plasticized with different types of plasticizers. Each plasticized TACs contained the same plasticizer content of 12 wt%. TAC/TPP film began to be softened at the lowest temperature. In contrast, TAC/BDP film had highest softening temperature. TAC/TPP/BDP film was in between TAC/TPP and TAC/BDP. The change of Tg in the plasticized TAC

TABLE 1 Characterizations of TAC Films with Different Types of Plasticizers

	Mechanical property					Optical property			
Instruments	UTM			DMA		UV		RETS-100	
						Transmittance (%)			
Samples	E (MPa)	TS (MPa)	EB (%)	E′ (MPa) at 25°C	Tg (°C)	400 nm	620 nm	Re (nm)	Rth (nm)
Neat TAC	55.0	155.0(±7.7)	28.3(±6.5)	3484	206.7	92.5	92.8	1.22	39.0
TAC/TPP 6 wt%	54.2	153.7(±8.1)	34.1(±6.3)	3578	184.8	89.1	90.9	0.42	55.7
TAC/TPP 12 wt%	52.5	147.8(±5.4)	35.0(±5.5)	4468	173.6	88.6	90.4	0.63	61.5
TAC/TPP 15 wt%	49.2	133.5(±4.5)	40.2(±2.5)	4117	171.8	88.5	89.9	0.35	64.1
TAC/TPP 20 wt%	47.8	127.4(±4.6)	48.3(±3.2)	3168	169.4	90.4	91.5	0.51	54.2
TAC/BDP 6 wt%	50.0	137.9(±7.1)	32.2(±6.1)	3529	197.7	91.6	93.0	0.49	57.0
TAC/BDP 12 wt%	47.5	126.4(±2.6)	32.7(±3.1)	3491	185.9	91.3	93.0	0.49	54.7
TAC/BDP 15 wt%	34.4	125.1(±8.0)	38.6(±6.3)	3909	186.7	89.9	91.4	0.53	57.2
TAC/BDP 20 wt%	31.7	122.2(±7.3)	40.8(±3.2)	2312	174.5	90.0	91.6	0.59	54.1
TAC/TPP-BDP 6 wt%	53.3	139.6(±5.9)	34.1(±3.7)	3843	194.8	90.6	91.5	0.54	54.7
TAC/TPP-BDP 12 wt%	49.2	136.0(±5.7)	34.3(±3.4)	3673	176.2	89.8	91.3	0.59	57.4
TAC/TPP-BDP 15 wt%	45.8	129.6(±7.5)	39.4(±6.2)	2626	178.6	90.5	92.1	0.47	57.4
TAC/TPP-BDP 20 wt%	44.7	122.4(±6.6)	41.6(±5.6)	2270	168.9	90.3	91.6	0.67	61.4

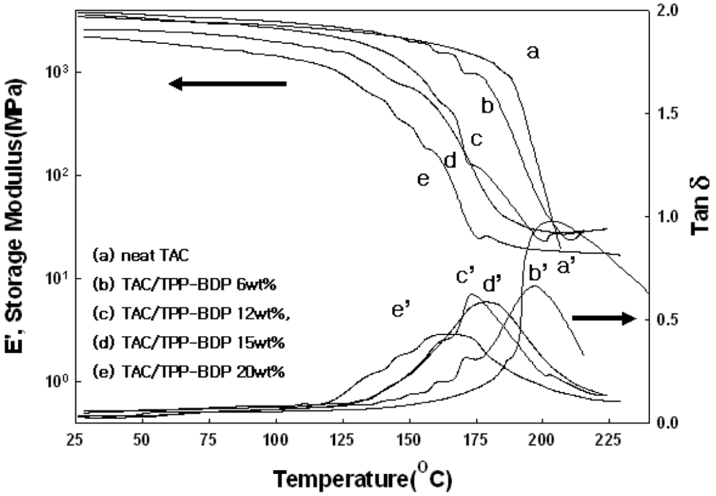


FIGURE 3 Storage modulus and tan δ curves of dynamic mechanical analyzer on the (a) neat TAC, (b) TAC/TPP-BDP 6 wt%, (c) TAC/TPP-BDP 12 wt%, (d) TAC/TPP-BDP 15 wt% and (e) TAC/TPP-BDP 20 wt% films.

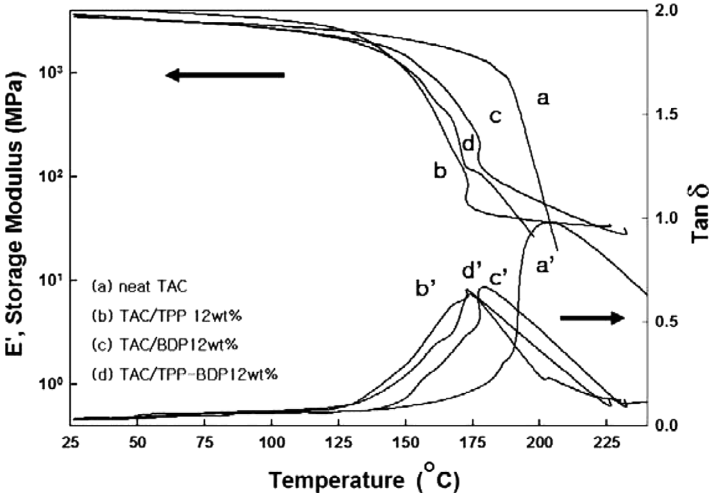


FIGURE 4 Storage modulus and tan δ curves of dynamic mechanical analyzer on the (a) neat TAC, (b) TAC/TPP 12 wt%, (c) TAC/BDP 12 wt% and (d) TAC/TPP-BDP 12 wt%.

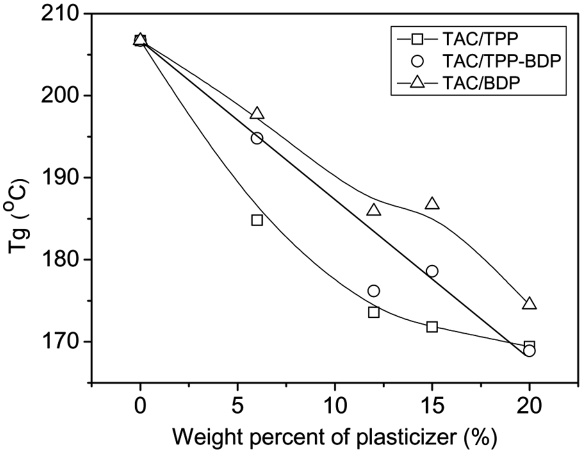


FIGURE 5 The change of glass transition temperature of TAC films as a function of plasticizer level.

films with various plasticization levels was shown in Figure 5. TAC/TPP had the largest decrease in Tg and TAC/BDP shows the smallest decrease in Tg at the same plasticizer level.

Figure 6 shows TGA curves of neat TAC, plasticizers and the plasticized TAC films. Neat TAC began to be degradated at around 350°C.

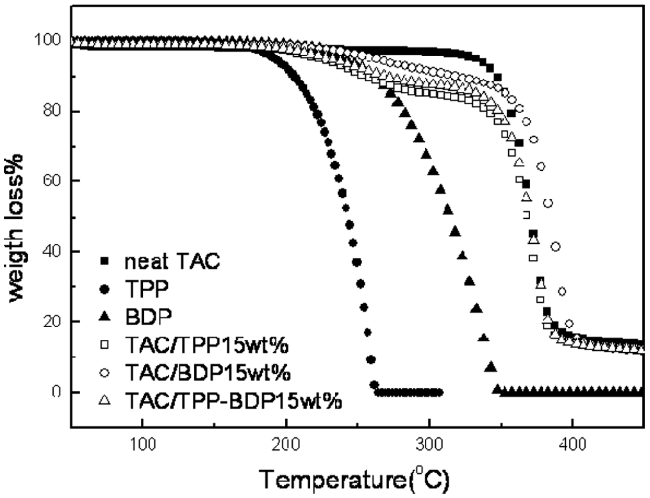


FIGURE 6 TGA thermographs of neat TAC, TPP, BDP, TAC/TPP 15 wt%, TAC/BDP 15 wt%, TAC/TPP-BDP 15 wt%.

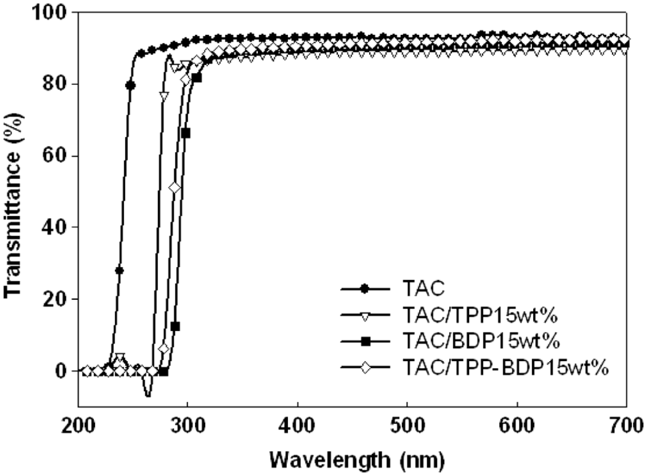


FIGURE 7 UV curves of neat TAC, TAC/TPP 15 wt%, TAC/BDP 15 wt% and TAC/TPP-BDP 15 wt%.

TPP began to lose weight before 200°C and BDP did not show the significant weight loss up to 250°C. As expected, TAC film plasticized with BDP had better thermal resistance than that with TPP. TAC with a mixture of TPP and BDP showed the intermediate thermal stability.

Figure 7 shows UV spectra of TAC films with various types of plasticizers. Plasticizer level was 15 wt%. All TAC films had good optical transmittance higher than 88% in the visible region ranging from 400 nm to 700 nm as listed in Table 1. Interestingly, the plasticized TAC film absorbed some of UV light below 300 nm thanks to the plasticizers.

Figure 8 shows optical measurement results of TAC/TPP/BDP films with various plasticizer levels. Retardation is generally described by birefringence × film thickness. In-plane retardation, Re and out of plane retardation, Rth of films are defined as following eqns:

$$\mathrm{Re} = (\mathrm{n_x} - \mathrm{n_y}) \times \mathrm{d} \tag{1}$$

$$\mathrm{Rth} = ((\mathrm{n_x} + \mathrm{n_y})/2 - \mathrm{n_z}) \times \mathrm{d} \tag{2}$$

where d is film thickness and z direction represents normal direction to the film surface. Re was measured at the measurement angle of

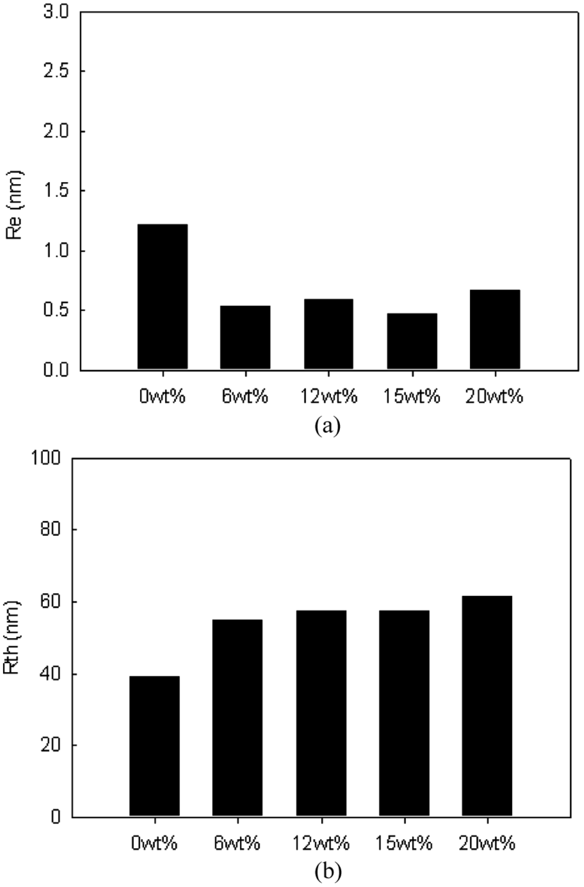


FIGURE 8 (a) In-plane retardation, Re and (b) out of plane retardation, Rth of TAC/TPP-BDP films with various plasticizer levels.

zero. All TAC/TPP/BDP films had very small Re value less than 1.2 nm, indicating that difference between in-plane refractive indices, $n_x - n_y$ was as low as at the order of 10^{-5}. Rth was around 50 nm. Re and Rth for a series of TAC/TPP and TAC/BDP films were summarized in Table 1.

SUMMARY

Moderate mechanical properties, thermal stability, optical transparency and optical isotropy of TAC films are essentially required in order to be used as a protective film for a polarizer in LCD application. Basically, neat TAC needs to be plasticized because of its brittleness without any deterioration of optical properties. Triphenyl phosphate (TPP), biphenyldiphenyl phosphate (BDP) and a mixture of TPP and BDP were investigated as a candidate of plasticizer for TAC. Optical transmittance and optical isotropy of the TAC films were good for the protective film, regardless of the type and contents of plasticizer. However, mechanical properties such as modulus, tensile strength and elongation at break, and thermal property were significantly affected by the type of plasticizer. TPP worked as the most effective plasticizer for TAC, because TAC/TPP had the largest decrease in Tg at the same plasticizer level. In addition, TAC/TPP showed the largest tensile strength and elongation at break at the same plasticizer level. It is representing that TPP made TAC being soft and tough at the expense of minimum decrease in hardness. However, TPP had very low evaporation temperature, which can not verify thermal stability for TAC protective film. BDP was more effective for thermal stability rather than for mechanical properties. A mixture of TPP and BDP achieved the compromising plasticization of TAC in mechanical properties and thermal stability for TAC protective film.

REFERENCES

[1] Rustemeyer, P. (2004). *Macromol. Symp.*, *208*, 1.

[2] Sata, H., Murayama, M., & Shimamoto, S. (2004). *Macromol. Symp.*, *208*, 323.

[3] Peterson, M. A. & Lipkowitz, K. B. (1997). *Jounal of Molecular Structure (Theochem)*, *395*, 411.

[4] Nakayama, H., Fukagawa, N., Nishiura, Y., Yasuda, T., Ito, T., & Mihayashi, K. (2006). *J. Photopolym. Sci. Technol.*, *19*, 169.

[5] Peter, Zugenmaier (2004). *Macromol. Symp.*, *208*, 81.

[6] Kim, K., Kim, J., Bae, J., Hong, S., & Kim, H. (2002). *Polymer.*, *43*, 2249.