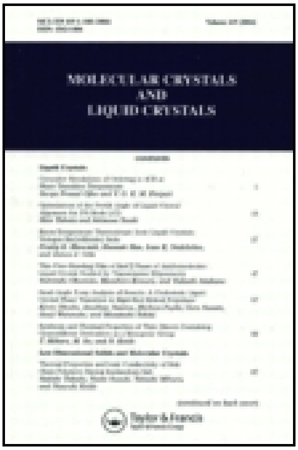

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Effect of Molecular Weight on the Mechanical and Optical Properties of Triacetyl Cellulose Films for LCD Applications

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Physical and optical properties of a series of TAC films with different molecular weight synthesized by acetylation of cotton linter have been investigated. The synthesized TACs had fully acetylated structure in which acetic acid contents was about 62%. Dimensional stability, thermal stability, modulus, tensile strength and elongation at break of TAC film were influenced by the molecular weight of base resin and they increased with the molecular weight. TAC films had good transparency as well as optical isotropy. Especially, optical property and moderate physical properties for protective film application in LCD were achieved above the molecular weight of 250 kg/mol.

Keywords: acetylation; LCD; polarizer; triacetyl cellulose

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INTRODUCTION

Acetyl cellulose is one of the oldest polymers synthesized in the middle of nineteenth century from natural cellulose by heating with acetic anhydride. Nevertheless, it still plays a key role in the field of fiber and textile industries, photographic film applications, flat panel display application, cigarette filter, separation and purification applications [1–3]. Although cheaper other synthetic polymers have been gradually replacing acetyl cellulose in many applications, total cellulose acetate demand is fast growing because of rapid market growth of triacetyl cellulose (TAC) film for a polarizer in LCD displays [2,4].

Especially, TAC films have been exclusively used as protective films for polarizing plate, because high transparency and optical isotropy of TAC film allows polarized light to pass it without any disturbance. TAC protective films have to sandwich the polarizing elements consisting of iodine or dyes absorbed on polyvinylalcohol (PVA) in order to prevent the uniaxially oriented PVA from shrinking and to prevent the iodine or dyes from evaporation. It also has to have moderate mechanical properties, thermal stability and dimensional stability [2].

TAC has been known as a crystalline polymer with crystallinity of about 25–30% processible by solution casting, not by melt processing because melting temperature is higher than onset temperature of degradation [5]. True physical properties of TAC films such as T_g, T_m, crystallinity are hard to measure because they are significantly influenced not only by degree of acetylation but also preparation conditions. In addition, few academic researches have been reported because most studies on the TAC film have been carried out by industry demand.

In this paper, we synthesized a series of triacetyl cellulose with different molecular weight by acetylating high quality cotton linters. Physical properties and optical properties of TAC films with different molecular weight have been investigated. We will discuss the reason why the molecular weight of TAC base resin influences on physical properties and optical properties in the academic point of view.

EXPERIMENTAL

Materials

A series of cotton linter cut and classified by the distance from the seed were used as a resource of cellulose to synthesize a series of TAC with different molecular weights. The used high grade cotton linter had more than 98% cellulose contents. Other chemicals such as acetic acid, acetic anhydride, and sulfuric acid, methylene chloride and methanol were purchased from Aldrich.

Synthesis of TAC

TAC is synthesized by acetylation of high-quality cotton linter. The polar hydroxyl alcohol groups of cellulose in cotton linter were substituted by acetyl groups in the hot mixture of acetic acid, acetic anhydride and sulfuric acid at 80°C. The esterification is in equilibrium with the reverse reaction, hydrolysis. The course of the reaction is mainly dependent on the water content. However, due to the fact that acetylation is performed with a slightly excess of anhydride, there is practically no water in the system, no reverse reaction take place and almost quantitatively triacetylcellulose is the reaction product [6]. A series of TAC with different molecular weight have been synthesized using a series of cotton linters which classified by the distance from the cotton seed.

Preparation of Solution Cast TAC Films

TAC polymer was dissolved in a mixed solvent consisting of the rate of nine to one methylene chloride and methanol. The TAC solution was filtered with a SUS filter in order to remove impurities and aged for 2days 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 20 minute drying at 80°C and finally 1hour drying at 110°C. Average thickness of the prepared films was about 80 μm. Sample name TAC100 K represented the TAC film prepared using TAC resin with the molecular weight of 100 kg/mol.

Measurements

Degree of acetylation of synthesized TAC is represented by acetic acid contents, which is measured by titration method in which TAC was hydrolyzed in hot 1 N NaOH alkali condition and excess NaOH was back-titrated using phenolphthalein indicator and 1 N H2SO4. Acetic acid contents was calculated by Eqn. (1).

$$\text{Acetic acid contents} = (\text{Blank} - \text{titaration weight}) \times 6.005/\text{sample weight} \tag{1}$$

Molecular weight and distribution of TAC resins were measured by GPC (TS Science- Jasco) using methylene chloride as a solvent and polystyrenes as standards. ^{1}H-NMR was measured by Oxford 600 MHz NMR using deuterated methylene chloride as a solvent. Differential scanning calorimetry was performed on a METTLER-TOLEDO DSC832e under nitrogen with heating rate of 10°C/min. Thermal mechanical analysis was measured by TMA 2940 at heating rate of 10°C/min. Thermalgravimetry analysis was performed by TA instrument TGA 2950 under nitrogen with a heating rate of 20°C/min. 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. Optical transmittance was evaluated by UV spectrophotometer (HP HEWLETT PACKARD 8453). Optical isotropy represented by Re and Rth values was measured by SCD-2000 R.

RESULTS

Molecular weight and molecular weight distribution of triacethylcellulose (TAC) synthesized by acetylation of a series of cotton linters were measured by GPC and listed in Table 1. Four types of TAC resins with different molecular weights of 100, 250, 270, and 330 kg/mol were synthesized by changing the reaction temperature. Lower reaction temperature made higher molecular weight. And higher molecular weight TAC had broader molecular weight distribution. Degree of acetylation in TAC is very important to measure because physical properties of TAC are very sensitive to the degree of acetylation. Degree of acetylation listed in Table 1 was determined by back-titration method being described in the experimental. If acetyl groups are fully substituted for all three hydroxyl groups in a repeat unit of cellulose, acetic acid contents are 62.5% [5]. The four types of TAC had the same acetic acid content about 62% indicating that every TAC was almost fully acetylated.

Figure 1 shows representative ^{1}H-NMR spectrum of the synthesized TAC. Insect describes chemical structure of TAC. Each peak is assigned in Table 2. Three signals of the methyl protons 7H, 8H, 9H were observed. It indicates that hydroxyl groups of cellulose in TAC were successfully substituted acetyl groups by acetylation [7]. Degree of substitution of acetyl group can be also calculated by integration

TABLE 1 Chemical Shifts of ^{1}H- NMR Signals for TAC

Signal	1H	2H	3H	4H	5H	6H	6'H	7H	8H	9H
δ/ppm	4.98	4.33	4.33	3.48	4.70	4.01	3.67	2.03	1.87	1.94

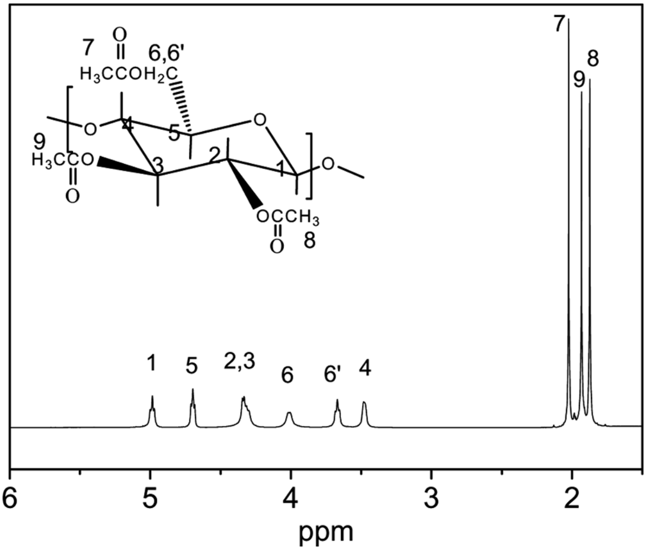


FIGURE 1 Chemical structure and ^{1}H- NMR spectrum of representative synthesized triacetylcellulose (TAC).

ratio of acetyl groups in NMR. It is consistent with the result of degree of acetylation measured by titration method.

Figure 2a shows DSC curves of representative cast TAC film. The sample was first-heated from room temperature to 230°C with heating rate of 10°C/min and then cooled to room temperature and then second-heated again. At first heating, TAC had a broad endothermic peak at around 60°C, a little valley near 180°C and an exothermic peak at around 200°C. In contrast, at second heating, the film clearly had one second order transition at around 180°C. In order to verify second order transition, auxiliary solid lines were drawn. An endothermic peak at the first heating is thought to be associated with the evaporation of some volatiles such as water and any residual solvents, because TAC tends to adsorb water and the film was

TABLE 2 Characterizations of the Synthesized TACs with Various Molecular Weights

Mw	100 K	250 K	270 K	333 K
Acetic acid contents	62.1	61.6	61.9	61.6
Degree of polymerization	169.2	270.0	316.5	380.2
Mw/Mn	4.3	8.6	9.1	10.9

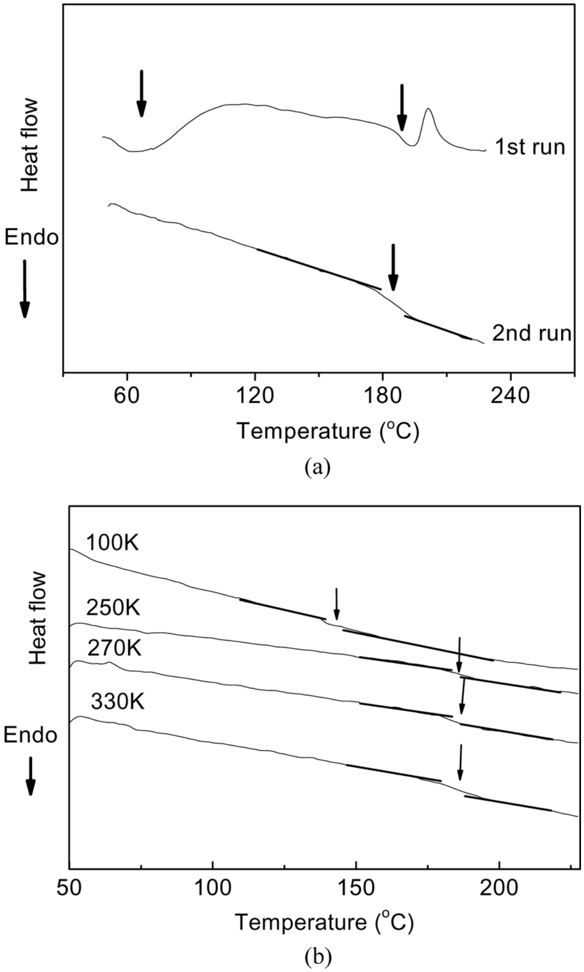


FIGURE 2 DSC curves of (a) 250k at the 1st and 2nd heating scans and (b) various TAC films with different molecular weights.

solution-cast. The slope change near 180°C appearing at the both heating scans must stem from a glass transition of TAC. And the origin of the exothermic peak was not clear yet. Figure 2b shows the DSC curves of TAC films with different molecular weights. Data were collected from 2nd heating. Each film had one clear glass transition temperature listed in Table 3. The glass transition temperature increased with the molecular weight. TAC100 K had lowest T_g around 137°C and other three TAC films had the T_g around 180°C.

TABLE 3 Characterizations of the Solution Cast TAC Films with Various Molecular Weights

Molecular weight	100 K	250 K	270 K	330 K
UTM				
Tensile Modulus (MPa)	15.8	22.5	22.9	23.4
Tensile strength (Mpa)	52.4	130.7	135.1	140.6
Elongation at break (%)	6.3	17.2	19.4	21.5
DMA				
E' at 25°C (MPa)	3884.4	4220.5	4243.9	4605.4
E' at 80°C (MPa)	3378.7	3791.7	3827.4	4073.4
E' at 120°C (MPa)	3624.8	3338.5	3345.9	3507.3
T_g (°C)	187.1	210.4	201.6	205.4
DSC				
T_g (°C)	137	177.5	180.1	187.4
UV transmittance				
at 400 nm	77.4	89.5	88.9	88.5
at 700 nm	91.8	91.3	91	90.9

Figure 3 shows the WAXS patterns of TAC 250k annealed at various temperatures. Each sample was annealing for 2 hours at the annealing temperature. TAC is almost in amorphous state at low temperatures. However, after annealing above 200°C, several characteristic crystal peaks were developed. It indicates that crystallization appeared at the high temperature. Therefore, high temperature endothermic peak in DSC must be from the crystallization.

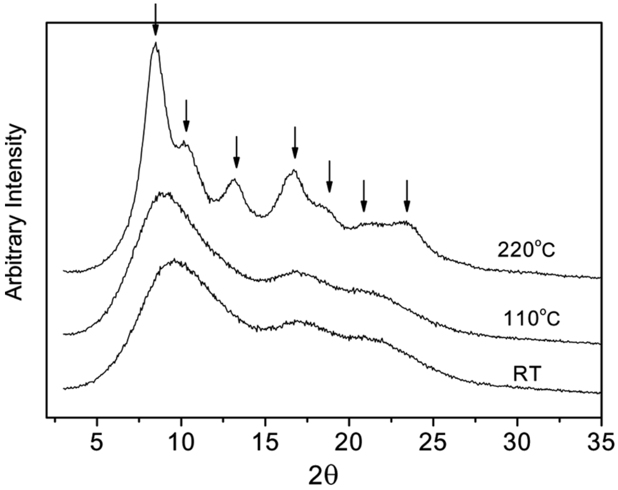


FIGURE 3 WAXS patterns of TAC 250k annealed at various temperatures.

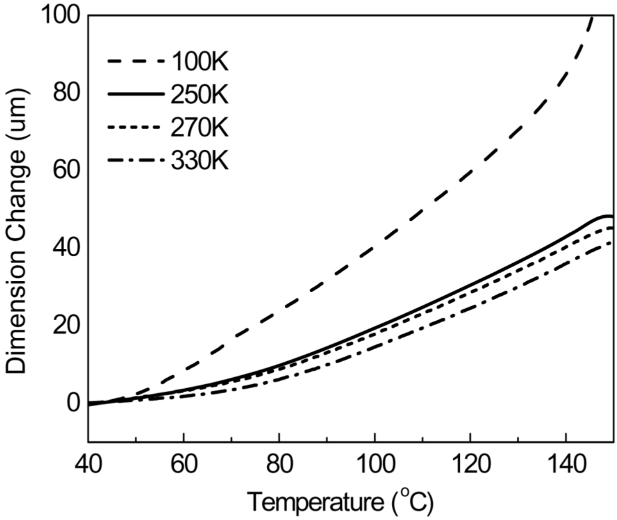


FIGURE 4 TMA curves of TAC films with different molecular weights.

Figure 4 shows TMA curves of a series of TAC films with different molecular weight. TAC100 K film showed the biggest thermal expansion as the temperature increases. Higher molecular weight TAC had the smaller thermal expansion. It indicates that dimensional stability of TAC film increases with the molecular weight.

Figure 5 shows TGA curves of various TAC films. TAC100 K with lowest molecular weight showed the worst thermal stability. It started

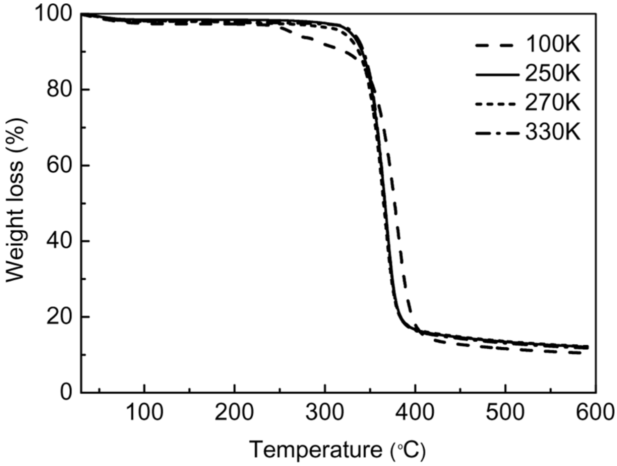


FIGURE 5 TGA thermographs of TAC films with different molecular weights.

to be degradated from the pretty low temperature of about 230°C. The others had similar degradation onset temperature at around 320°C.

Figure 6a shows representative Stress-Strain curves of TAC films with various molecular weights. TAC film was uniaxially drawn to machine direction (MD) as well as transverse direction (TD), respectively. MD was corresponding to the moving direction of bar coater. Most TAC films showed sharp and linear increase in tensile stress up to yield point appearing at the small strain of about 5% and then slow increase until the break point occurred around 20%. However, TAC100k showed the most brittle behavior and was ruptured right after yield point. Figures 6b and 6c shows the tensile strength and elongation at break of TAC films. Tensile strength depended on the molecular weight, not on the coating direction. As the molecular weight increased, TAC film showed sharp increase in tensile strength up to 250 K and then slow increase with molecular weight. In contrast, elongation at break depended on the molecular weight as well as the

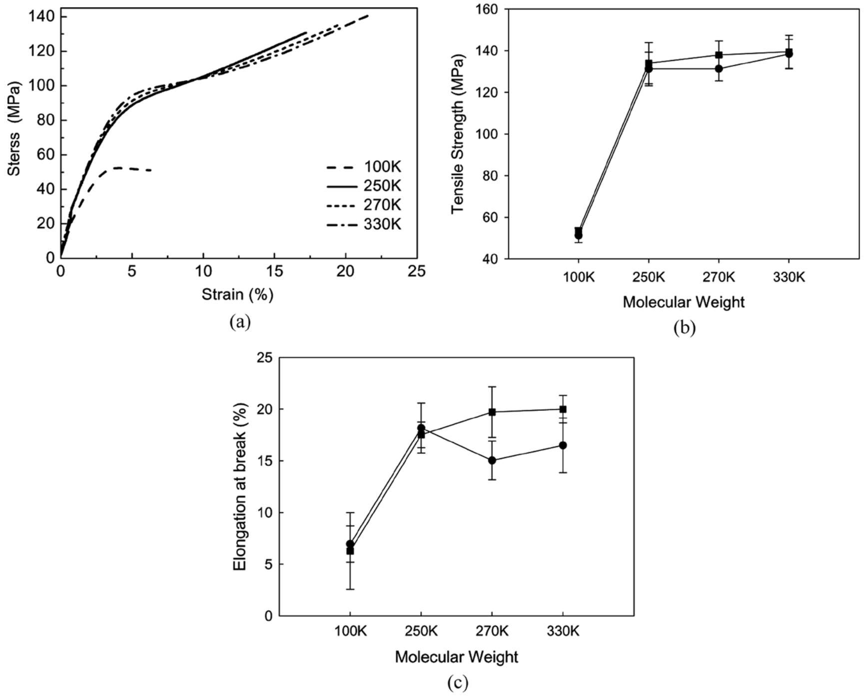


FIGURE 6 (a) Stress-Strain curves, (b) tensile strength and (c) elongation at break of TAC films with different molecular weights drawn to TD direction (–■–) and MD direction (–●–).

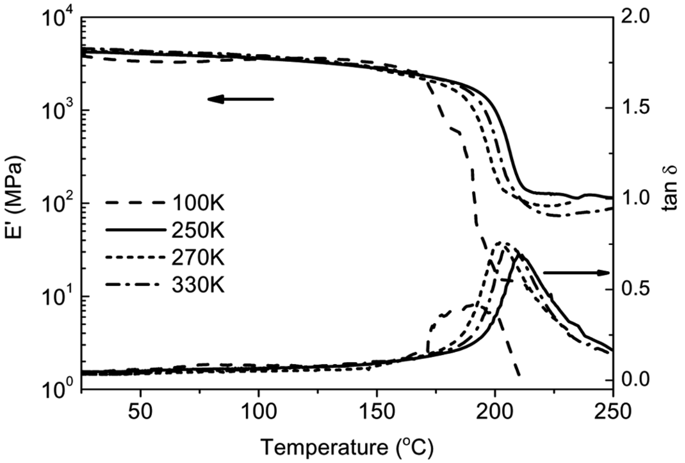


FIGURE 7 Storage modulus and damping factor of DMA investigation of TAC films with different molecular weights.

extension directions. Elongation at break had the same molecular weight dependence as tensile strength. But elongation at break of TAC films with high molecular weight was affected by extension direction. Drawing to TD showed higher elongation at break than drawing to MD. Average tensile properties were listed in Table 3. Average tensile modulus, tensile strength and elongation at break also increased with the molecular weight.

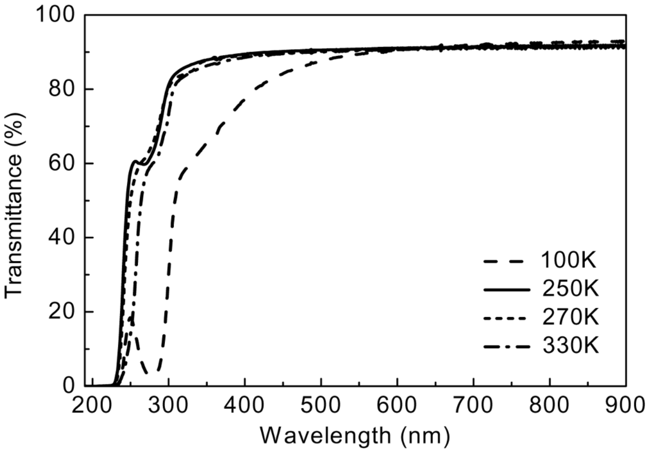
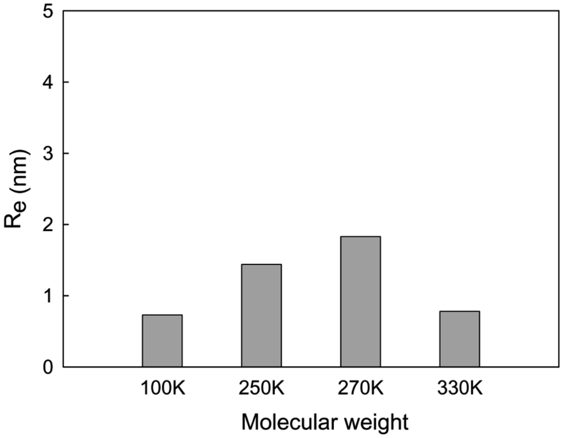
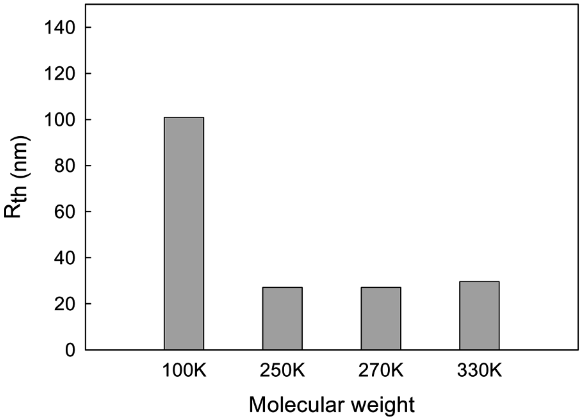


FIGURE 8 UV spectra of TAC films with different molecular weights.



(a)



(b)

FIGURE 9 (a) In-plane retardation (Re) and (b) out of plane. retardation (Rth) of TAC films with different molecular weights.

Figure 7 shows storage modulus and damping factor of TAC films with different molecular weights. Storage modulus (E′) represents the stored elastic energy and the damping factor $\tan \delta = E''/E'$ is more related with the dissipation of energy. Storage modulus of TAC films at three different temperatures were listed in Table 3. Storage modulus slowly decreased with the temperature until a steep drop appeared at the glass transition. As the molecular weight increased, storage modulus increased except TAC100k especially at around 100°C. At the intermediate temperature around 100°C, TAC100k had higher storage modulus than others. Glass transition temperature was determined by the maximum point of damping factor. TAC100k had lowest glass transition temperature of 187°C and others had the glass transition temperature around 205°C.

Figure 8 shows UV spectra of TAC films with different molecular weights. TAC films had pretty good optical transmittance higher than 90% in the visible region ranging from 400 nm to 700 nm except TAC100 K in the blue color range. Transmittance of TAC films at 400 nm and 700 nm listed in Table 3.

Figure 9 shows optical measurement results of TAC films with different molecular weights. Retardation is generally given by birefringence × film thickness. In-plane retardation, Re and out of plane retardation of film, Rth are defined as following eqns:

$$\mathrm{Re} = (n_x - n_y) \times d \tag{2}$$

$$\mathrm{Rth} = ((n_x + n_y)/2 - n_z) \times d, \tag{3}$$

where d is film thickness and z direction represents plane normal direction of the film. All TAC films had very small Re value less than 2 nm regardless of molecular weight, indicating that difference between in-plane refractive indices, n_x–n_y was as low as at the order of 10^{-5}. Most TAC films also had moderate Rth of about 30 nm except TAC 100 K with Rth of 100 nm.

DISCUSSIONS

TAC is known as a crystalline polymer with crystallinity of about 25–30%. But crystallographic diffraction of cast TAC films was very blunt in Figure 3. It indicates that cast TAC film is in the amorphous states. A glass transition temperature of TAC film was able to be measured by DSC in Figure 2 and DMA in Figure 7. T_g of TAC films increased with the molecular weight. In DSC measurements, one can observe an unknown exothermic peak right above T_g. In Figure 3, it is observed that dull diffraction pattern of as-cast film become sharper in WAXS patterns after high temperature annealing. It was strongly supporting that the exothermic peak in DSC was from crystallization. However, it was impossible to measure Tm before onset temperature of degradation of 250°C. That is the reason why TAC film can only be prepared by solution casting, not by melt processing.

Thermal and dimensional stability and tensile properties of TAC films increased with the molecular weight. The tensile properties showed sharp increase up to 250 K and then slow increase in molecular weight. It could be explained by end group effect and chain entanglement. TAC with higher molecular weight can form more tightly entangled structure than that with smaller molecular weight. In addition, smaller molecular weight promotes bigger end group effect which tends to enhance degree of freedom. Therefore, TAC100 K film with lowest molecular weight showed the worst thermal and dimensional stability and the most brittle behavior under the uniaxial extension.

Interestingly, elongation at break of TAC films with high molecular weights of 270 K and 330 K was influenced by drawing direction in Figure 6c. Drawing to TD made higher elongation at break than drawing to MD. Polymer chains tend to lie in plane within the film and higher molecular weight of a polymer induces slower chain mobility during the solvent evaporation of solution casting. Therefore, polymer chains with higher molecular weights are likely to be oriented to the coating direction in the plane of the film so that they seem to have drawing direction dependency on the extensibility.

Optical transparency and optical isotropy of TAC film are key properties for the protective films in LCD. Transmittance, and In-plane retardation, Re and out of plane retardation, Rth were used as measures of optical transparency and optical anisotropy, respectively. Regardless of molecular weight, the synthesized TAC films kept good optical transmittance higher than 90% in visible region. The films showed very small Re value less than 2 nm, almost no birefringence, even though TAC with high molecular weight showed anisotropy of elongation at break in uniaxial tensile test. TAC has big intermolecular free volume because of the existence of bulky acetyl groups. The acetyl carbonyl groups in TAC are oriented perpendicular to the polymer backbone. Therefore, TAC can exhibit low in-plane birefringence even when the polymer chains are slightly oriented in the plane of the film.

CONCLUSION

Physical and optical properties of a series of TAC films with different molecular weight synthesized by acetylation of cotton linter have been investigated. The synthesized TACs had fully acetylated structure in which acetic acid contents were about 62%. Dimensional stability, thermal stability, modulus, tensile strength and elongation at break of TAC film were influenced by the molecular weight and increased with the molecular weight. The synthesized TAC films had good transparency as well as optical isotropy. Especially, optical property and moderate physical properties for protective film application in LCD were achieved above the molecular weight of 250 K.

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