Reducing the environmental load of triacetyl cellulose film production using wood pulp

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ABSTRACT: Triacetyl cellulose (TAC) films, which are currently produced mainly from cotton linter, are widely used for liquid crystalline display (LCD) applications. However, cotton linter is an expensive source of cellulose and the environmental load related with cotton cultivation is notoriously heavy. Herein, the replacement of cotton linter by wood pulp was systematically investigated to explore the possibility of TAC production using a less expensive source. The mechanical and thermal properties of TAC films made from wood (wTAC) were outstanding compared to those of TAC films made from cotton (cTAC). The optical transparency of wTAC was also excellent. While Tinuvin (a UV stabilizer) produced more isotropic structures in cTAC films, it produced more anisotropic structures in wTAC films. Overall, the optical films of wTAC showed good performance for LCD applications, comparable to that of cTAC. These results could be used to develop more environmentally friendly production methods for optical TAC films. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42146.

INTRODUCTION

In recent times, growing concerns related to the global environment have reactivated research on natural polymers and their modification. Such research has been boosted by modern chemistry and processing technologies.[1–4] However, the use of natural polymers does not necessarily guarantee a decrease on the environmental load in related industries. Instead, we must carefully examine the environmental load involved in the production of natural polymers; sometimes, serious environmental concerns are associated with natural polymers. Cotton, a source of cellulose, is an example.

Cellulose is the most common macromolecule in nature and has been optimized over eons of evolution.[5,6] It has strong inter- and intramolecular interactions with tunable hydrophilicity, which enable it to have a diverse range of properties.[7–9] As a natural consequence, cellulose has demonstrated excellent applicability in various industries.[10] However, one drawback related with cellulose materials is that they can be difficult to process.[11] The polymerization and dissolution of cellulose is not straightforward, and the whole cellulose industry relies on natural sources for its backbone chains.[12] The different sources of cellulose, such as cotton, wood, bacteria, and other vegetables, usually have different chemical and physical identities. Therefore, different sources provide different materials properties for use in final applications.[13,14] The chain architecture and three-dimensional chain organization of cellulose vary depending on its source, resulting in significant variations in its properties.

Using side-group substitution with various molecules, a wide range of cellulose materials is currently commercially available.[15,16] One such example is triacetyl cellulose (TAC).[17–20] This is the best material for optical films for liquid crystalline display (LCD) applications because it has good thermal stability and a proper hygroscopic coefficient.[21] Owing to TAC's high melting temperature and the requirement of low birefringence, solvent casting is the most common preparation method used to make optical films. This preparation method can inhibit anisotropy in the chain orientation, resulting in low (almost zero) birefringence.[22]

Currently, all TAC films for LCD applications are produced from cotton linter. This material satisfies the complex requirements of optical, mechanical, and thermal properties.[4,23] However, cotton should no longer remain as the material of choice for this application. In addition to its disadvantageously high price, there are also serious environmental problems associated with cotton. These environmental concerns are largely related to the heavy use of toxic chemicals during cotton processing.

Cotton farming has been described as a war against insects.[24] According to the Environmental Justice Foundation (EJF), cotton consumes 16% of the world's insecticides, including nerve agents and neurotoxins, despite the fact that it covers only 2.5% of the world's cultivated land.[25] Insecticide poisoning is a direct cause of many deaths, and long-term exposure to these chemicals has been shown to cause birth defects, nervous disorders, and skin and eye problems.[26] The pesticides applied to cotton also affect the water quality of the surrounding cultivation areas. For example, 240,000 fish were killed in Alabama (USA) in 1995 after heavy rain washed pesticides into surrounding bodies of water (UN Food and Agriculture Organization report, 2001). Even with the recent introduction of genetically modified cotton, most farmers still apply pesticides in the same way; the risks of acute poisoning remain the same.[27]

Herein, we report the first investigation on the possibility of utilizing wood pulp as a natural source for optical TAC films for LCD applications. Wood pulp is common and inexpensive and has few associated environmental concerns. Systematic comparisons between TAC from cotton linter (cTAC) and TAC from wood pulp (wTAC) were made, and the effects of common necessary additives (i.e., plasticizers and UV stabilizers) on the mechanical, thermal, and optical properties of the films were discussed in detail.

EXPERIMENTAL

Materials

TAC obtained from cotton linter (cTAC, flake, $M_w = 331$ kg/mol, $M_w/M_n = 3.23$, 122.9 cPs (6 wt %)), and TAC from wood pulp (wTAC, flake, $M_w = 345$ kg/mol, $M_w/M_n = 3.52$, 132.0 cPs (6 wt %)) were purchased from Eastman Kodak (USA). Methylene chloride (EP 99.5%) from Daejung Chemical & Metals (Kyunggi-Do, South Korea), triphenyl phosphate (T, plasticizer, 99%) from Sigma Aldrich (USA), ethylphthalylethylglycolate (E, plasticizer, 93%) from Tokyo Chemical (Kangseo, South Korea), Tinuvin (UV, UV stabilizer, 98%) from BASF (Germany), and methanol (HPLC, 100%) from J.T. Baker (USA) were used without purification (Figure 1).

Film Preparation

TAC (10 wt %) was first dissolved into a mixed solvent of methylene chloride and methanol (9 : 1 wt ratio) and stirred for 24 h. When T and E were used, their content was 10 wt % of TAC, and the content of UV was 1 wt % of TAC. After filtering (SUS filter, Fine Science, South Korea, pore size 3 μm, SUS303), the solution was sealed and aged at 5°C for 2 days, and then casted onto a precleaned glass plate using a doctor blade (SI, UK, 250 mm wide). The films (17 × 22 cm) were dried in a three-step process with an 8-mm-tall glass cap as
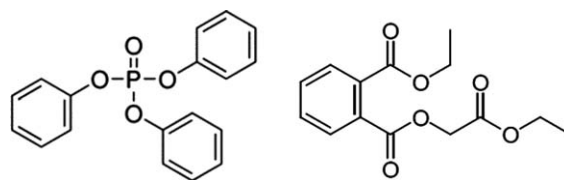

Figure 1. Chemical structures of plasticizers (left: T and right: E).

follows: 1) at RT for 4.5 h, 2) at 80°C for 30 min, and 3) at 110°C for 2 h. This process resulted in the formation of uniform films that were 60 μm thick.

Characterization

^{1}H-NMR (NMR 600 MHz, Oxford Instruments, UK), employing chloroform-d (Cambridge Isotope Lab., MA, USA, D 99.8%) as a solvent, and an FT-IR spectrometer (Nicolet iS10, Thermo Fisher Sci., USA) were used to analyze the cast film samples. The mechanical properties of films (70 × 10 mm for UTS and 6.3 × 30 mm for DMA) were measured with a universal testing machine (UTS, H5KT, Tinius Olsen, USA, ASTM D638, 10 mm/min extension rate) and a dynamic mechanical analyzer (DMA Q800, TA Instrument, USA, N_2 atmosphere, 5°C/min heating rate, from 0 to 250°C, 1 Hz). A differential scanning calorimeter (DSC Q20, TA Instrument, USA) scanned samples (2–3 mg) twice at 10°C/min (heating and cooling) from 30 to 300°C under an N_2 atmosphere (no annealing step). A thermogravimetric analyzer (TGA Q50, TA Instrument, USA) was used to scan the samples (2–3 mg) from 30 to 600°C at 10°C/min under an N_2 atmosphere.

The optical transmittance of 2.5 × 2.5 cm films was measured by a UV spectrophotometer (JASCO V-670, Japan), and the optical isotropy of the 5 × 5 cm films was measured by a retardation inspection system (RETS-100, Otsuka, Japan). In-plane retardation (R_e) and out-of-plane retardation (R_{th}) are defined as follows: $R_e = (n_x - n_y) \times d$ and $R_{th} = ((n_x + n_y)/2 - n_z) \times d$, where n is the refractive index, d is the film thickness, and z is the direction perpendicular to the film surface.[28] The thermal expansion coefficient was measured by a thermomechanical analyzer (TMA 2940, TA Instrument, USA) under an N_2 atmosphere at 10°C/min.

RESULTS AND DISCUSSION

Regarding the raw materials, wTAC is known to be less crystalline and have less α-cellulose content and more alkylester side groups than cTAC.[29] After the film processing, the two materials become almost amorphous. With the addition of the small molecules (T, E, and UV, which are necessary additives), the properties of TAC films became unpredictable. The two different sources of TAC showed almost identical NMR and FT-IR results (SI). Both TACs (wTAC and cTAC) have the same cellulose backbone.[30]

The molecular weight and glass transition temperature of wTAC are similar to those of cTAC (Table I). The tensile moduli of both films were also similar. In our previous investigation, the tensile modulus and glass transition temperature reflected an increase in the molecular weight of the TAC films.[19] The similar values of the glass transition temperature lead us to presume

Table I. Properties of TACs Made from Wood and Cotton

	wTAC	cTAC
Molecular weight (kg/mol)	350	330
Modulus (GPa)	2.7	2.7
Glass transition temperature (°C)	208	209
Thermal expansion coefficient (μm/m°C)	MD 58	MD 66
	TD 62	TD 51
α-Cellulose %	97.0	99.8
Degree of substitution (acetyl groups)	3.0	3.0

MD, machine direction; TD, transverse direction.

that the entanglement densities of the two TACs are probably quite similar. The similar modulus values further support this conjecture. However, the results of the thermal expansion coefficient show distinct differences (Table I). This is a property of the films that reflects the 3D chain organization and architecture formed during the film casting, and could be closely related to the intrinsic chain structures. The optical properties of the films can also be related to the chain architecture and organization.

Figure 2 shows the typical stress–strain behavior of films of different compositions under uniaxial tensile mode. The plasticizing effects of T and E are discernible as a general trend in the typical stress–strain curves, particularly above 3% strain, i.e., a lower tangential modulus and larger strain to break induced by the addition of T and E. An interesting comparison can be made regarding the effect of the different cellulose sources. While wTAC and cTAC themselves show no differences, they develop significant differences with the addition of plasticizers and UV stabilizer: wTAC/T-E,UV shows a distinctly higher tan-
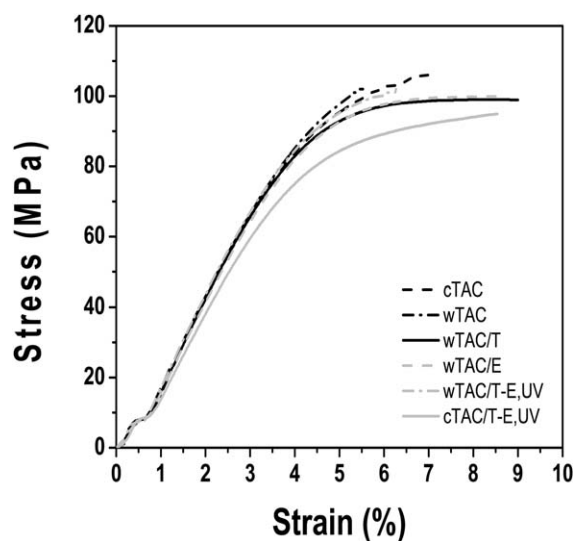

Figure 2. Stress–strain curves of wTAC and cTAC films with and without plasticizers (T and E) and UV stabilizers (UV) under uniaxial stretching.
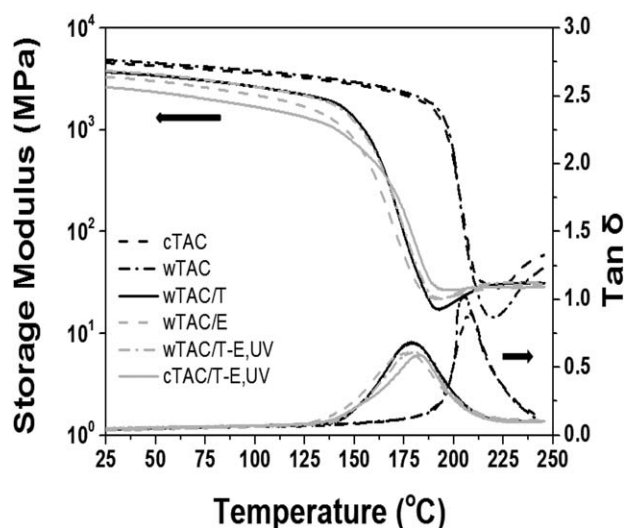

Figure 3. DMA results of wTAC and cTAC films showing the T_g and storage moduli.

gential modulus relative to that of cTAC/T-E,UV, as shown in Figure 2. The yield stress also appears to be higher. The addition of these small molecules (T, E, and UV) can increase the free volume of cellulose chains by inserting into stacked chains, and the intrinsic organized chain structures of the casted films will strongly interact with this addition, resulting in an amplification of the effects of the different intrinsic chain structures. However, no dramatic changes in Young's modulus were noticed (wTAC = 2700 MPa; cTAC = 2700 MPa; wTAC/T = 2600 MPa; wTAC/E = 2600 MPa; wTAC/T-E,UV = 2700 MPa; and cTAC/T-E,UV = 2400 MPa), and the yield stress is rather difficult to compare in detail (even the 0.2% offset yield).

As indicated in Table I, the T_g obtained from DSC does not significantly reflect the different cellulose sources. Consistently, DMA results in Figure 3 show similar T_g values in the samples of the two TACs. wTAC has a relatively large glass transition peak compared to cTAC, which is an important intrinsic difference. With the addition of T, E, and UV, the T_g decreased to 175 ~ 180°C (from 205 ~ 210°C), showing the significant plasticizing effects of the small molecules. In Figure 3, the storage moduli also reflect the plasticizing effects. cTAC/T-E,UV shows a significantly lower storage modulus than all the other samples, and wTAC/T-E,UV shows a relatively excellent storage modulus compared to cTAC/T-E,UV. The storage modulus values in Figure 3 largely follow the same trends shown in Figure 2.

The lowered modulus and T_g, caused by the incorporation of the small molecules, can be accompanied by a lowered heat resistance. Figure 4 shows that weight loss starts significantly earlier with the addition of small molecules (210°C), while both wTAC and cTAC tolerate thermal energy up to 330°C. After the first weight loss (10–20 wt %), the samples with small molecules show a second weight loss at 330°C. Therefore, the first weight loss seems to be related with the small molecules. However, the amounts of weight loss do not directly reflect the amounts of the small molecules (10 + 1 wt %, Supporting Information Figure S3). Thermal degradation,
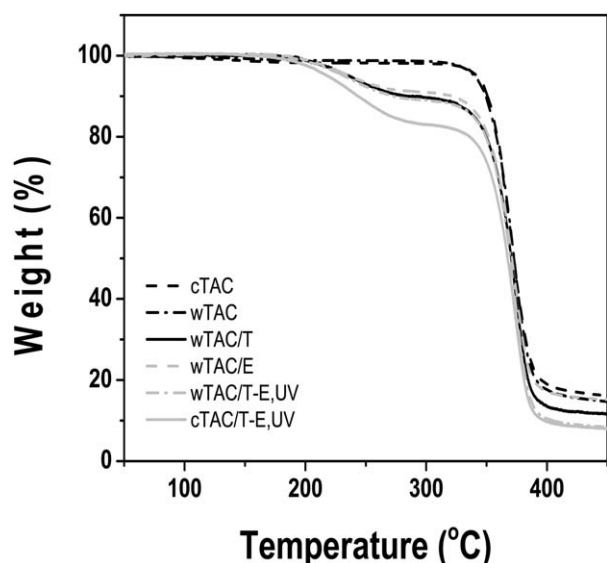
Figure 4. TGA results of wTAC and cTAC films with and without plasticizers (T and E) and UV stabilizers (UV).

Figure 6. In-plane optical retardation of wTAC and cTAC with and without plasticizers (T and E) and UV stabilizers (UV).

which occurred by a cooperative mechanism between small molecules and the main chains, seems to be involved in the first weight loss. In Figure 4, cTAC/T-E,UV shows a distinctly lowered heat resistance, which is consistent with the results of Figures 2 and 3. Therefore, the inexpensive wTAC/T-E,UV continues to demonstrate unexpectedly outstanding thermal stability compared to cTAC/T-E,UV. The differences in the char contents by the addition of the small molecules were as large as ca. 10 wt %.

So far, the addition of the small molecules produced different effects in the properties of the TACs. Particularly, wTAC/T-E,UV showed surprisingly superior properties to cTAC/T-E,UV. Alternatively, cTAC/T-E,UV, a typical formulation for LCD applications, shows distinctly lowered properties in its uniaxial
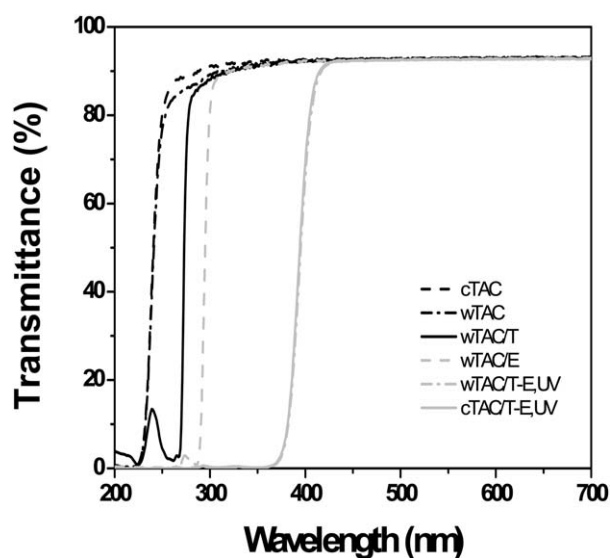
tensile modulus, storage modulus, and thermal gravitational properties. Will the same trends remain in the optical properties of the films? We found relatively good performance for wTAC while analyzing its transparency and optical retardation.

Figure 5 provides the transparency results. In the visible light range, all the films showed excellent transparency. After the addition of T and E, a slight decrease in transparency in the UV range is identified. The further addition of the UV stabilizer successfully blocks the transmittance of light in the UV range. Meanwhile, the addition of both plasticizers and UV stabilizer maintains film transparency above 400 nm. Overall, the transparency curves of wTAC/T-E,UV and cTAC/T-E,UV are identical, implying that replacing wTAC with cTAC does not inhibit film transparency.

Figure 5. Light transmittance properties of wTAC and cTAC with and without plasticizers (T and E) and UV stabilizers (UV).

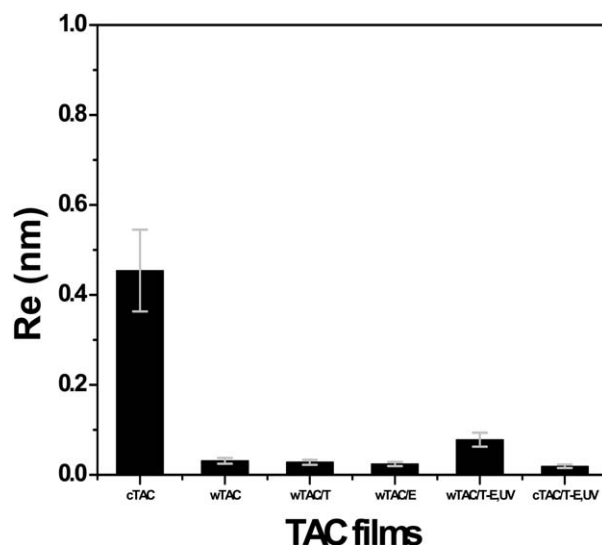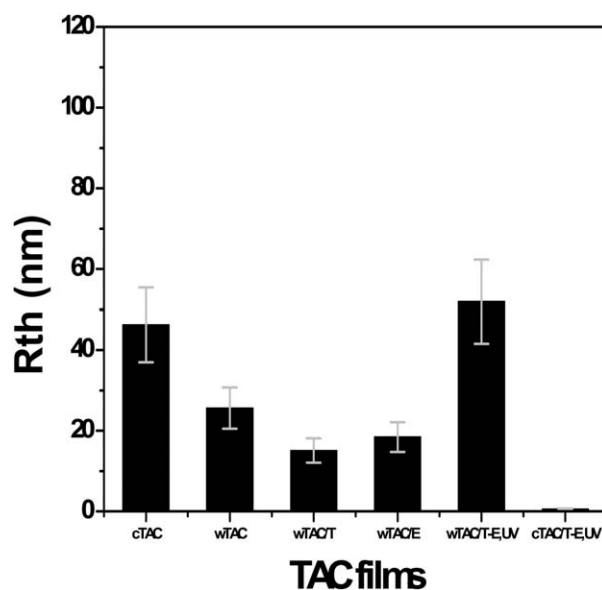**Figure 7.** Out-of-plane optical retardation of wTAC and cTAC with and without plasticizers (T and E) and UV stabilizers (UV).

Figures 6 and 7 provide the results of the optical retardation measurements. First, one can see that wTAC has much lower retardation values than cTAC. As discussed above, this is possibly due to the lower α-cellulose and greater number of alkylester side groups. Additionally, the UV stabilizer has a different influence on the molecular chain organization during solvent casting in the two cases. The R_e value of wTAC/T-E,UV is smaller than that of the cTAC, but larger than that of cTAC/T-E,UV. The optical retardation (R_e) of cTAC, which was originally large, was significantly reduced by the introduction of T, E, and UV, indicating more isotropic chain organization (cTAC and cTAC/T-E,UV).

The molecular chains of raw cTAC organize into anisotropic phases, which have a degree of molecular chain orientation, resulting in a relatively large R_e value. The small molecules (T, E, and UV) seem to break these interactions and significantly decrease the optical retardation. Conversely, the introduction of the same set of small molecules into wTAC, which originally has a small R_e value, unfortunately triggered an increase in the optical retardation, indicating more anisotropic chain orientation. However, this value is still much smaller than that of cTAC. In detail, the plasticizers (T and E) did not lead to a major increase in the optical retardation. Instead, this increase is ascribable to the addition of UV.

Similar results can be found in the out-of-plane optical retardation (R_{th}), shown in Figure 7. The addition of small molecules (T, E, and UV) distinctly reduced R_{th} in the cases of cTAC, but increased R_{th} in the cases of wTAC. As conjectured from Figure 6, in wTAC, R_{th} was increased mainly by the addition of UV. In fact, the introduction of T and E decreased R_{th}, but this decrease was completely cancelled out by the addition of UV, resulting in a higher R_{th} value in the case of wTAC/T-E,UV. Therefore, the optical retardation of wTAC seems to be the only remaining point for the future development; these results will lead us to investigate different UV stabilizers to achieve better performance in wTAC films in the future.

The intrinsic mechanical and thermal properties of wTAC and cTAC were indiscernible. Even their transparency properties were indiscernible. However, the two TAC materials were discernible in their anisotropic properties (i.e., their optical retardation and thermal expansion coefficients), which is explained by the differences in their molecular structures.

For the performance of optical TAC films, TAC should employ plasticizers and UV stabilizers[4]. Interestingly, the effects of the small molecule addition significantly depend on the type of matrix. With the addition of the small molecules, the use of wTAC has advantages in terms of thermal and mechanical properties, but disadvantages in terms of optical retardation (when compared to cTAC). The effect of the small molecules on the optical retardation was reversed in the case of cTAC. The different numbers of alkylester side groups in wTAC and cTAC might be the main reason for the varying effects of the small molecules. These results could be related to the different solubility and processability of cellulose materials, which have been previously studied.[31] It is possible that the small molecules are less disruptive in the molecular chain alignment for wTAC, which could provide strengthening effects and increase the optical

retardation. More detailed molecular interaction studies between TAC chains and the small molecule additives are necessary to properly design the final compositions of wTAC optical films in the future.

CONCLUSIONS

TAC optical films prepared from wood pulp can reduce the environmental load related with cotton farming as well as the price load related with cotton linter. wTAC showed excellent mechanical and thermal properties compared to cTAC, particularly after the addition of plasticizers and UV stabilizers. The optical transparency of wTAC was also outstanding compared to cTAC. However, its optical anisotropy requires further improvement; the use of an inadequate UV stabilizer increased both the in-plane and out-of-plane optical retardation values. This study clearly shows the possibility of using wTAC as a replacement for cTAC, which is widely used in LCD applications.

ACKNOWLEDGMENTS

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