Assessment of the composition and condition of animation cels made from cellulose acetate

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ABSTRACT

Cellulose diacetate and cellulose triacetate cels from animated feature films in the collection of the Walt Disney Animation Research Library were tested by several analytical techniques in order to assess their composition and look for evidence of degradation. Triphenyl phosphate and a range of phthalate plasticizers were identified using pyrolysis-gas chromatography/mass spectrometry, which also showed evidence that evaporation of more volatile plasticizers may have occurred. Plasticizer content measurements by solvent extraction, found to be more accurate than volatile content data from thermogravimetric analysis, revealed there was less residual plasticizer in triacetate cels compared to diacetate cels. Gas chromatography/mass spectrometry, performed to quantify the acetyl content of cels after removal of plasticizers by solvent extraction, revealed some evidence for hydrolysis of the oldest cels, although the reduction could be related to original variations in acetate content from the polymer manufacturers. Use of Fourier-transform infrared spectroscopy to measure deacetylation of the cellulose acetate polymer based on the hydroxyl to carbonyl peak area ratio proved less satisfactory. Moreover, because the cels cannot be measured directly due to interference from plasticizers, non-invasive assessment of deacetylation using a portable instrument would be impossible. The results from this analytical survey provide an important point of reference against which long-term changes in cel composition can be monitored.

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1. Introduction

Animation cels are thin, transparent plastic sheets onto which subjects are painted or drawn in order to create sequences of images for animated motion picture productions. Historically, the first plastic support used in animation was celluloid, developed at the end of the 19th century as a support in photography, which is composed of cellulose nitrate plasticized with camphor [1,2]. Despite its good flexibility and dimensional stability, cellulose nitrate is highly flammable and subject to hydrolytic, thermal and photochemical deterioration processes that lead to the release of hazardous gases. During the 1920s, these limitations led to the gradual replacement of cellulose nitrate by cellulose acetate (CA), which was subsequently used throughout the 20th century. Cellulose acetate was originally considered to be an excellent archival material due to its lack of flammability, yet proved to be susceptible

to deterioration through hydrolysis, migration and loss of plasticizer and photodegradation [2—4]. Although polyester became more prevalent in the 1990s due to its superior chemical and dimensional stability [4—6], cellulose acetate was never completely abandoned in animation production because many animators preferred the way CA accepted the black ink of the line drawings [2,3].

To better understand the issues related to studying and preserving cellulose acetate animation cel collections, it is helpful to review the chemistry of this important industrial plastic. Acetylation of cellulose is the process of replacing the hydroxyl groups on highly-refined cellulose, of which there are three per ring unit, with acetyl groups by treatment with acetic anhydride in the presence of catalysts such as sulfuric acid and zinc chloride [3,5,7]. Full acetylation of cellulose produces cellulose triacetate (CTA), which has three acetyl groups per cellulose ring and a degree of substitution (DS) of three. Cellulose diacetate (CDA) is produced by partial hydrolysis of CTA to the desired degree of substitution. The most common DS in CDA polymers is 2.5 due to the improved solubility in common solvents, molecular weight and physical properties of

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the final product [3,7,8]. Catalysts are also removed during this process, which improves the stability of the final product.

An alternative term used in manufacturing to express the degree of substitution of CA polymers is the % acetyl content. The relationship between % acetyl and DS is shown in Equation (1):

$$DS = (3.86 \times \% \, acetyl)/(102.4 - \% \, acetyl) \qquad (1)$$

Based on Equation (1), a DS of 3 is equivalent to 44.8% acetyl, a DS of 2 is equivalent to 34.9% acetyl, and a DS of 1 is equivalent to 26.5% acetyl. Cellulose triacetate with acetyl content between 43.7% and 44.8% is often known as *primary cellulose acetate*, whereas partially-hydrolyzed cellulose acetate is commercially-labeled as *cellulose acetate* if the acetyl content is between 37% and 40%, and *high-acetyl cellulose acetate* if the content ranges between 40% and 42%. *Cellulose acetate* with acetyl content between 38.7% and 40.1% is preferable for the production of fibers, films and lacquers, whereas high-acetyl cellulose acetate is more difficult to process [9].

Because cellulose acetate is brittle and thermally decomposes before it reaches its softening point, plasticization is needed to reduce the glass transition temperature of the polymer matrix and improve the physical properties such as workability, flexibility and tensile strength [9–11]. In the early days of CA production, many additives were tested in an attempt to find effective plasticizers. The main characteristics of appropriate plasticizers are compatibility with the polymer and permanence in the matrix. It was discovered that mixtures of alkyl phthalates and triphenyl phosphate produced suitable plastic products [5]. Phthalate esters such as dimethyl phthalate and diethyl phthalate yielded a good overall balance of properties, whereas phosphates imparted flame retardancy [11]. Because moldable cellulose acetate may contain 20–40% by weight of plasticizers, they play an important role in the long-term stability of CA films [3,7].

In the 20th century, cellulose acetate was used widely for numerous industrial, commercial and design art products, as a medium for sculpture, and perhaps most importantly as a photographic film base. Given the intrinsic historic, social and cultural value of these objects, much research was carried out to study cellulose acetate degradation and develop preservation strategies. It was found that exposure to moisture, heat, or acids leads to deacetylation, release of acetic acid and eventual reversion back to cellulose. Initially, the acetic acid stays trapped in the plastic matrix, but slow migration to the surface gives rise to the phenomenon known as "Vinegar Syndrome" [1,2,4]. Moreover, hydrolytic degradation of triphenyl phosphate leads to the production of phosphorous acid that, like acetic acid, catalyzes the deacetylation process and causes polymer chain scission [2–4]. Another concern is photodegradation, which is associated with the generation of radicals due to the absorption of light in the far UV region and leads to yellowing and embrittlement [3,8]. Finally, migration and evaporation of plasticizers leads to shrinkage and embrittlement [12].

Research by the Image Permanence Institute (IPI) showed that, although there is no practical way of stopping or reversing deterioration of photographic film made from cellulose acetate, rates of deterioration can be substantially reduced by lowering the temperature and relative humidity in storage areas, and by using sorbents in microenvironments to remove off-gassed acetic acid. Levels of acetic acid in storage microenvironments can be monitored through the use of acid detection strips, which indicate the onset of vinegar syndrome by a color change [13]. These precautions should also be broadly applicable for preserving other objects made from cellulose acetate.

Animation art archives abound in cellulose acetate materials that, over time, may exhibit loss of mechanical integrity and change in visual appearance. One of the largest collections of animation cels is at the Walt Disney Animation Research Library (WDARL), which contains over 200,000 cels made from cellulose nitrate, cellulose acetate and polyester. No special environmental considerations were taken for storing the cels until 1989, when the collection was relocated to air conditioned storage areas. Since 1999, the cels have been stored between 62 and 65 °F and at 50% relative humidity in vaults equipped with carbon filtration, which is broadly consistent with IPI recommendations for film. According to the IPI research, further extension of the lifetime of the CA plastic should be achievable by reduction in the temperature and relative humidity of the storage areas, however, the impact on delamination and flaking of the cel paints has not been determined.

Information about the type of cel plastic, the range in % acetyl content and the variability in the composition and content of the plasticizers would provide an important baseline of information needed to better understand the present composition of the cel plastics, against which their composition can be monitored in relationship to changes made to the storage environment. Yet this information was not available in the archives because the cel collection had never before been analyzed.

As a first step towards developing an understanding of the specialized storage conditions needed to preserve for cellulose acetate animation cels, scientific analysis was performed on selected animation cels from the WDARL with production dates ranging from 1937 to 2003 using several invasive and non-invasive techniques. Fourier-transform infrared spectroscopy (FTIR) was used for polymer identification. Plasticizers were identified by means of pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS). The plasticizer content was quantified gravimetrically by solvent extraction, and compared to the results from thermogravimetric analysis (TGA). Finally, the acetyl content was measured quantitatively [14] using gas chromatography/mass spectrometry (GC/MS), and compared to the results of FTIR.

2. Experimental

2.1. Extraction of plasticizer and isolation of CA polymer from cels

A first attempt at plasticizer extraction was based on the chemical method described by Stannett [5], which consisted in dissolution of the cel in acetone and flocculation of cellulose acetate polymer by adding a 1:1 solution of aqueous methanol followed by 1% aqueous ammonium chloride. This method was found to be effective on cellulose diacetate, but failed to fully dissolve cellulose triacetate.

Optimum results were obtained by following the extraction procedure of Whitnack and Gantz [15] that involved the use of a 1:1 mixture of hexane and absolute ethyl alcohol as extraction solvent, in which both CDA and CTA are insoluble. In order to accelerate the process, the procedure was modified by omitting the use of the Soxhlet extractor. Samples roughly 1 mg in weight were cut into small fragments and left in the solvent for 48 h at 38 °C, after which the liquid was collected and the cellulose acetate polymer films left to dry overnight at 38 °C. The cel samples were weighed before and after the solvent extraction procedure in order to measure the plasticizer content.

2.2. Volatile content from thermogravimetric analysis of the cels

Thermogravimetric analysis was carried out to determine the percentage weight loss of volatile components from the cel samples. Cel samples were prepared by punching out a single disk of film, which weighed approximately 5 mg. Measurements were recorded using a Mettler Toledo TGA/SDTA851e, and STARe

software version 8.10. Empty crucible and sample weights were measured using the automated balance function in the software. After a 15 min isothermal period, the temperature was ramped from 30 °C to 450 °C at a heating rate of 5 °C per min^{-1}. Oxygen-free nitrogen purge gas was used at a flow rate of 50 ml min^{-1}. Based on evolved gas analysis studies of plasticized CA [16], the plasticizer content of the cels was defined as the weight loss between 30 °C and 280 ± 12 °C for CDA cels, and between 30 °C and 308 ± 3 °C for CTA cels. Weight losses during sample weigh-in were ignored in order to exclude adsorbed moisture from the plasticizer content results.

2.3. Plasticizer identification by pyrolysis-gas chromatography/ mass spectrometry

Cel samples were taken with a Harris uni-core punch of 0.5 mm diameter core size, placed into 50 μl stainless steel Eco-cups and loaded into an autosampler. Samples were pyrolyzed for 6 s at 550 °C in a Frontier PY-2020D pyrolyzer. The pyrolysis interface was at 320 °C. An Agilent 5975C inert MSD/7890A gas chromatograph/ mass spectrometer was used for analysis. Oven program: 2 min at 40 °C, then 20 °C per minute to 320 °C. Agilent DB-5MS UI column (30 m × 0.25 mm × 0.25 μm); 1 ml/min helium; split injection at 320 °C with 50:1 split ratio; MS interface at 320 °C; MS scan range 10–550 amu at 2.59 scans per second. Peak area percent reports of the plasticizers based on selected ion chromatograms were generated using Agilent Enhanced ChemStation software (rev. E.02.02). In general, plasticizers present below 5% of the total area were excluded from the data set. Table 1 lists information about the plasticizers identified in the cels.

2.4. Evaluation of the degree of acetylation

As mentioned previously, exposure to moisture, heat, or acids causes the polymer to hydrolyze, forming acetic acid and hydroxyl groups on the polymer chain [1,2]. Two methods were evaluated for estimating the degree of acetylation and degree of substitution of the animation cels. It should be noted that neither method can be used directly on the cels because the plasticizers interfere with the analytical results [3,6]. Instead, the methods were applied to the CA polymer residue remaining after solvent extraction of plasticizers from the cels.

2.4.1. Gas chromatography/mass spectrometry procedure

Aminolysis of CA using pyrrolidine converts acetyl groups to acetylpyrrolidine, which may be quantified using GC/MS [14]. After weighing 0.3–0.9 mg of CA into a crimp-top vial, 200 μl of a stock solution of pyrrolidine (Sigma–Aldrich) that contained 1000 ppm hexadecane as internal standard were added. The sealed vials were heated at 80 °C for 18 h, with vortex mixing after 3 h and again after 18 h. After cooling, the solutions were analyzed on an Agilent 6890/ 5973 inert GC/MS equipped with a Frontier Ultra ALLOY 1 capillary column (30 m × 0.25 mm × 0.5 μm) and Frontier Vent-Free
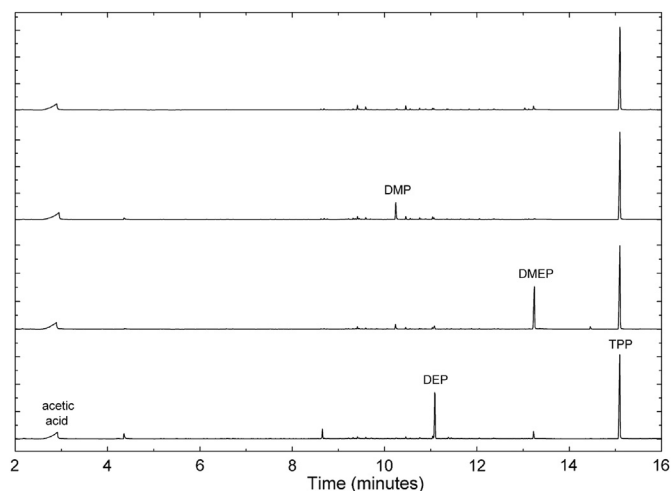

Fig. 1. Py-GC/MS results for selected animation cels showing plasticizers. Legend (from bottom to top): Jungle Book cel 2, The Aristocats cel B, Aladdin, The Great Mouse Detective cel B. Plasticizers identified from data in Table 1.

Adaptor. GC oven program: 80 °C for 1 min, 20 °C/min to 195 °C, 120 °C/min to 300 °C and 2.3 min isothermal. Helium at 0.4 m/s; split injection at 280 °C with a 50:1 split ratio; MS interface at 300 °C. The acetyl content of the samples was evaluated using a linear calibration curve forced through zero from standard solutions of acetylpyrrolidine (Tokyo Chemical Industry Company, Limited) ranging from 1000 to 10,000 ppm in pyrrolidine. The percent acetyl content may be calculated using Equation (2):

$$\% \text{ acetyl} = 38.02 \times (\text{ppm acetylpyrrolidine})$$
$$\times (\text{ml pyrrolidone})/(\mu\text{g cellulose acetate}) \qquad (2)$$

2.4.2. Fourier-transform infrared spectrometry procedure

Samples were prepared by flattening fragments of unplasticized cellulose acetate polymer onto a diamond window using a metal roller. The analysis was performed in transmission with a Bruker Optics Vertex 70 FTIR microscope with a nitrogen-cooled multi-band MCT detector. The spectra were collected using the software Opus version 6.5 over a range of 600–4000 cm^{-1}, with a 4 cm^{-1} resolution and 64 scans accumulation. Omnic version 7.1 software was used for manipulation of the spectra.

Polymers in the cels were identified using FTIR. The degree of acetylation was investigated by calculating the peak area ratio between the O–H stretching band at 3486 cm^{-1} and the C=O stretching peak at 1746 cm^{-1}. As CA hydrolyzes, loss of acetyl groups results in reduction of the C=O peak and increase in the O–H band [3,17].

2.5. Samples and standards

Archival records of the WDARL indicated cel suppliers switched from CDA to CTA in the early 1980s after meeting

Table 1
Plasticizers identified in Disney animation cels.

Chemical name	Common name	CAS number	ID	Time (min)	Quant. ion
1,2-Dimethyl benzene-1,2-dicarboxylate	Dimethyl phthalate	131-11-3	DMP	10.2	163
1,2-Diethyl benzene-1,2-dicarboxylate	Diethyl phthalate	84-66-2	DEP	11	149
3-Hydroxy-2,2,4-trimethylpentyl 2-methylpropanoate		6846-50-0	TXIB	11.1	71
Methyl 2-[(2-ethoxy-2-oxoethoxy)carbonyl]benzoate		85-71-2	MCMP	12.7	163
1,2-Dibutyl benzene-1,2-dicarboxylate	Dibutyl phthalate	84-74-2	DBP	13.1	149
1,2-Bis(2-methoxyethyl) benzene-1,2-dicarboxylate		117-82-8	DMEP	13.2	59
Ethyl 2-[(2-ethoxy-2-oxoethoxy)carbonyl]benzoate		84-72-0	ECMP	14.6	149
Triphenyl phosphate		115-86-6	TPP	15	326

rigorous standards of the animation industry regarding color, transparency and lack of optical imperfections. A total of 81 cels that originated from animated feature films dating from 1931 to 2003 were studied. A 15 cm strip removed from along the right edge of each cel supplied sufficient sample material for all of the tests (including mechanical studies of the cels that are not included in this paper). In general, each of the cels appeared to be in good physical condition across their entire area, with little or no perceptible wrinkling, color or odor of acetic acid. Due to the invasive nature of the sampling, only production cels with small, minimally significant painted images on them were selected for sampling. For comparative purposes, unplasticized reference standards of CDA and CTA polymers were obtained from Scientific Polymer Products and from Sigma–Aldrich. Standards of DEP and TPP plasticizers were obtained from Scientific Polymer Products.

3. Results and discussion

An overlay of selected results for Py-GC/MS analysis of CDA and CTA cels appears in Fig. 1. The peak for acetic acid, formed by side-chain elimination of the CA polymer, appears as a broad peak centered around 2.8 min. Plasticizers appear as sharp peaks with an order of elution that is roughly equivalent to their volatilities. Summaries of the plasticizer compositions based on Py-GC/MS analysis of the CDA and CTA cels appear in Tables 2 and 3, respectively. The distribution of plasticizers was found to correlate broadly to the type of CA polymer, and the earliest cels exhibited the greatest variety of plasticizers. In general, cellulose diacetate, which was used until 1981, contained primarily diethyl phthalate (DEP) and triphenyl phosphate (TPP), whereas dimethyl phthalate (DMP) and triphenyl phosphate (TPP) were the main plasticizers for cellulose triacetate, which was used from 1983 onward.

Table 2
Plasticizer content and compositions for cellulose diacetate animation cels from animated feature productions in the collections of the Walt Disney Animation Research Library. Groups of cels with similar plasticizer compositions are outlined with double line borders.

Animated production	Sample description	Date	Plasticizer peak area percentages							% Plasticizers	
			TPP	DEP	MCMP	TXIB	DMEP	ECMP	DMP	Solvent extraction	TGA
Snow White		1937		91					7	15	15
Fantasia	cel A	1940		39	57					14	19
Fantasia	cel B	1940		39	56					13	20
The Adventures of Ichabod and Mr Toad		1949	56	28				11		15	14
Pinocchio		1940	42	53							
Bambi	cel B	1942	61	38						13	13
The Song of the South		1946	49	48							
Cinderella	cel A	1950	65	29						15	25
Cinderella	cel B	1950	52	42						15	23
Alice in Wonderland	cel A	1951	56	40						17	14
Alice in Wonderland	cel B	1951	60	35						17	13
Peter Pan		1953	66	32						15	14
Lady and the Tramp	cel A	1955	60	38						14	13
Lady and the Tramp	cel B	1955	59	39						15	23
The Sleeping Beauty	cel A	1959	64	34						15	22
The Sleeping Beauty	cel B	1959	63	37						15	13
The 101 Dalmatians	cel A	1961	63	36						15	15
The 101 Dalmatians	cel B	1961	60	38						14	22
The Sword in the Stone	cel A	1963	61	38						14	11
The Sword in the Stone	cel B	1963	58	41							
Mary Poppins	cel A	1964	60	39						13	13
Mary Poppins	cel B	1964	62	36						15	12
The Jungle Book	cel 4 – Bagheera	1967	66	30							
Bedknobs and Broomsticks		1971	53	44						14	16
Bedknobs and Broomsticks	Ostrich cel	1971	53	44						17	14
Robin Hood		1973	55	43						15	16
Robin Hood	new cel – Sheriff	1973	59	39							
Robin Hood	Little John cel	1973	58	40						17	15
Winnie the Pooh & Tigger Too	cel B – Pooh	1974	59	38							
The Rescuers	cel A	1977	59	40						14	22
The Rescuers	cel B	1977	54	45						14	15
Pete's Dragon		1977	59	38						15	22
Pete's Dragon	Dragon cel	1977	60	36						15	23
The Fox and the Hound	cel A	1981	31	66						15	24
The Fox and the Hound	cel B	1981	29	67						15	22
The Fox and the Hound	Chief cel	1981	25	73							
The Fox and the Hound	Copper cel	1981	27	71							
The Jungle Book	cel 5 – Buzzie	1967	43	22	32			<5			
Winnie the Pooh & the Blustery Day	Eeyore cel	1968	44	11	40			<5		15	19
Winnie the Pooh & Tigger Too	cel A - Owl	1974	47	11	39			<5		16	18
The Jungle Book	cel 1 – Buzzie	1967	48	12	33			<5		14	20
The Jungle Book	cel 2 – Buzzie	1967	47	10	36			5		14	18
The Jungle Book	cel 3 – Buzzie	1967	52	9	32			5		15	19
The Aristocats	cel A	1970	50				40		6	15	21
The Aristocats	cel B	1970	51				38		5	21	20

Table 3
Plasticizer content and compositions for cellulose triacetate animation cels from animated feature productions in the collections of the Walt Disney Animation Research Library. Groups of cels with similar plasticizer compositions are outlined with double line borders.

Animated production	Sample description	Date	Plasticizer peak area percentages				% Plasticizers	
			TPP	DMP	DBP	DMEP	Solvent extraction	TGA
Mickey's Christmas Carol	Willie the Giant cel	1983	68	29			13	17
Mickey's Christmas Carol	Scrooge McDuck cel	1983	68	29			14	16
The Black Cauldron		1985	70	29				
Oliver & Company	cel A	1988	70	28			10	13
Oliver & Company	cel B	1988	72	26			10	13
Little Mermaid	cel B	1989	70	28			9	13
The Prince and the Pauper	cel A	1990	71	28			9	13
The Prince and the Pauper	cel B	1990	71	27			9	13
The Rescuers Down Under	cel A	1990	75	24			10	13
The Rescuers Down Under	cel B	1990	75	24			9	12
Beauty and the Beast		1991	70	28			10	13
Aladdin		1992	72	27			10	12
Mulan		1998	69	29			8	13
Brother Bear		2003	70	28			9	13
Pocahontas	cel A	1995	45		55		9	12
Emperor's New Groove		2000	56		44		8	12
Atlantis: The Lost Empire		2001	57		42		11	13
The Black Cauldron	Taran with sword cel	1985	88		<5	7		
The Black Cauldron	Witch Orwen	1985	88		5	7		
The Great Mouse Detective	cel A	1986	87		6	5	11	13
The Great Mouse Detective	cel B	1986	89		5	<5	11	13
The Great Mouse Detective	new cel – Ratigan	1986	88		5	<5		
The Lion King		1994	80			18	12	15
Hercules		1997	92			7	10	14
Fantasia 2000		2000	92			7	10	14
Little Mermaid	cel A	1989	91				11	13
Pocahontas	cel B	1995	98				10	12
The Hunchback of Notre Dame		1996	98					
Tarzan		1999	99				10	13
Lilo and Stitch		2002	99				8	13

In Tables 2 and 3, cels with similar plasticizer compositions were grouped together for clarity. Overall, six different plasticizer formulations were discovered in the CDA cels, and five in the CTA cels. It can be observed that plasticizer formulations did not strictly adhere to production date, and that different formulations appeared in cels made for the same feature film. Examples include the pairs of cels from 'Winnie the Pooh and Tigger Too' (dated 1974), 'The Jungle Book' (1967) and 'Pocahontas' (1995). Lot and batch variation for the CA sheets may account for these compositional differences in plasticizers within cels made for a given film. However, in the early days of the animation industry, before cels acquired greater commercial value and cultural significance, there was the practice of removing the ink and paint from cels created for earlier films and reusing them. This means that for a given cel sample in the tables, there may be a discrepancy between the film production date and the actual date of manufacture for the cel.

Another factor that can affect the plasticizer composition of cels is evaporation and loss of more volatile species. A recent study of cellulose acetate plasticized with diethyl phthalate [18] showed that the plasticizer content can be substantially reduced by heating to relatively low temperatures. This trend can be seen in Fig. 2, a graph of the peak ratio of DEP/TPP versus production date for selected CDA cels that contain only these two plasticizers. In this graph, TPP can be considered as a non-volatile component used essentially for normalization. Although the correlation coefficient is not high (0.2), there is nonetheless a recognizable trend towards reduction in the more volatile plasticizer with cel age. This indicates that, over time, one may expect subtle changes in the plasticizer composition of the cels, which may affect the resistance to hydrolysis of the cels due to changes in the hydrophobicity of the surfaces, as well as the dimensional stability.

It was also observed that the relative amount of TPP was quite variable within the set of cels, and some of the newest cels contain TPP as the sole plasticizer. The presence of TPP in the cels is significant because of its relationship to the degradation of objects made from cellulose acetate, which was shown to vary with TPP concentration [12].

Fig. 3 shows the plasticizer content measured by solvent extraction relative to the production date of the cels. The plasticizer
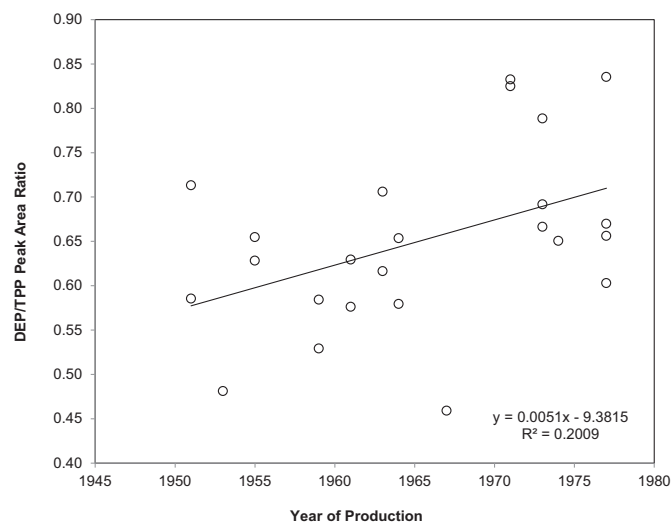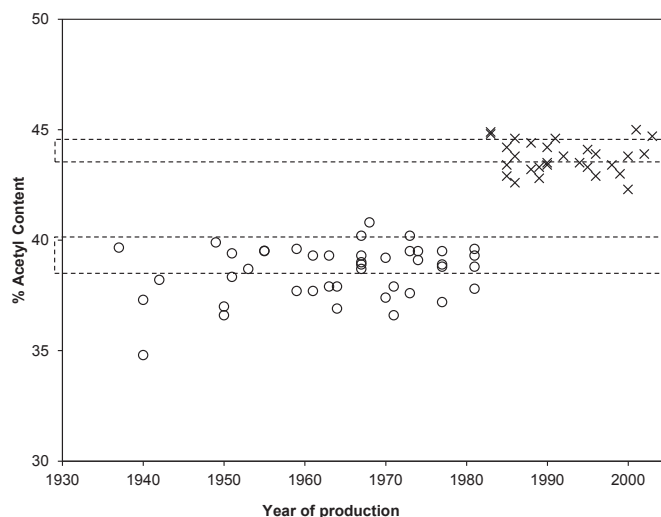

Fig. 2. Py-GC/MS results showing DEP/TPP peak area ratio versus year of production for animation cels.
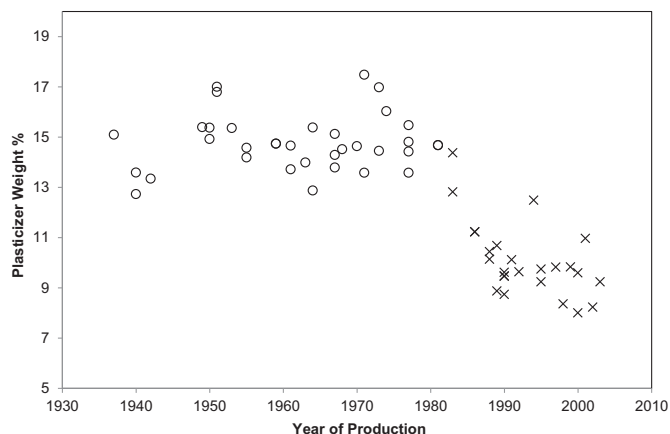
Fig. 3. Percent plasticizer content from solvent extraction procedure versus year of production for cellulose diacetate (○) and cellulose triacetate (×) cels.

Fig. 5. % acetyl content versus year of production for cellulose diacetate (○) and cellulose triacetate (×) cels.

content for CDA (used before 1981) ranges from 12 to 21%, whereas in cellulose triacetate, the plasticizer content ranges between 8 and 14%. This difference relates to the higher free volume of CDA compared to CTA, making it possible to accommodate more plasticizer. Thus, it is clear that a substantial portion of animation cels made from CA polymers is plasticizer. This fact must be taken into consideration when developing conservation treatments for animation cels that utilize solvents, such as the re-adhering of flaking paints.

Measurements of the plasticizer content of cels by means of the solvent extraction procedure proved to be a highly accurate based on the near total absence of residual TPP in the CA polymers after treatment. The solvent extraction procedure for measuring plasticizer content was found to be quite effective. In order to evaluate the extraction time needed to obtain pure cellulose acetate, periodic Py-GC/MS analyses were carried out to estimate the amount of plasticizer left at each step of extraction, and TPP proved to be the most strongly retained additive. After 48 h at 38 °C, the TPP levels were less than 0.5% of the initial amount. Thus, any traces of residual TPP should neither interfere with subsequent analysis, nor contribute significantly to the total mass of the CA polymer.

Using these results as reference data, thermogravimetric analysis was shown to be wholly inadequate for this measurement. For example, the plasticizer contents for CTA cels were overestimated by 33% using TGA, primarily because as CTA is heated, it begins thermal decomposition before TPP is fully volatilized from the cels (Fig. 4). Thus, weight loss from CTA decomposition contributes to the overall volatile content. In contrast, no clear trend was evident for the CDA cels. TGA underestimated the plasticizer content for nearly three-quarters of the CDA cels by 13%. This may be because the increased free volume of the CDA makes it more difficult to fully volatilize plasticizers during heating.

Measurement of the acetyl content by GC/MS proved to be both highly accurate and reproducible. Seven replicate analyses of the CDA standard, which contains 39.7% acetyl, yielded 39.4 ± 0.5% acetyl. Five replicate analyses of cel B from The Rescuers yielded 38.5 ± 0.6% acetyl. This level of accuracy is satisfactory for differentiating CDA from CTA.
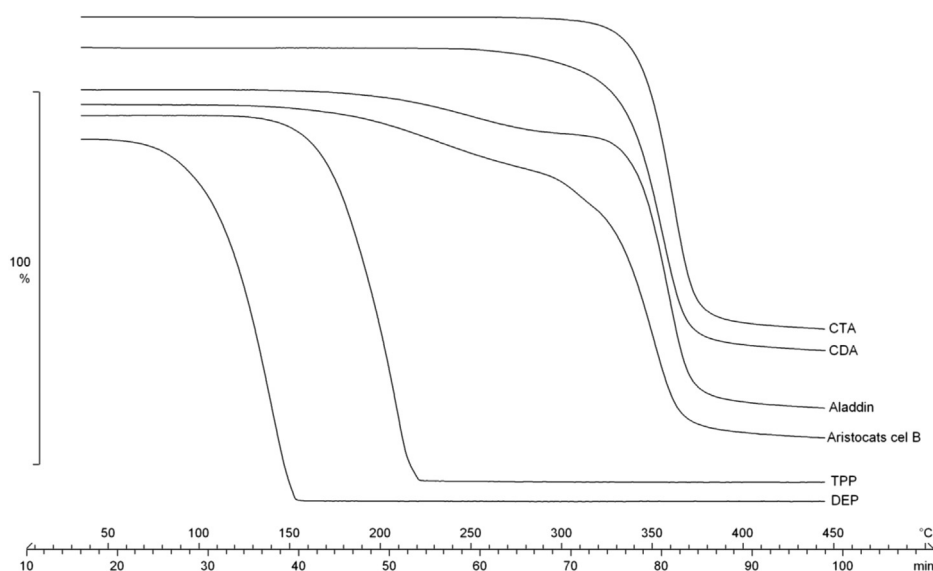
Fig. 4. Thermogravimetric analysis of DEP, TPP, CDA, CTA and selected animation cels.
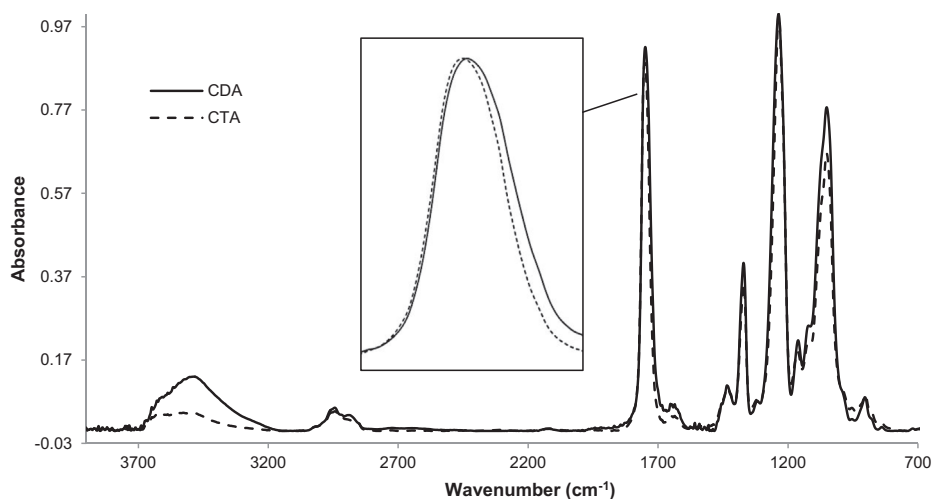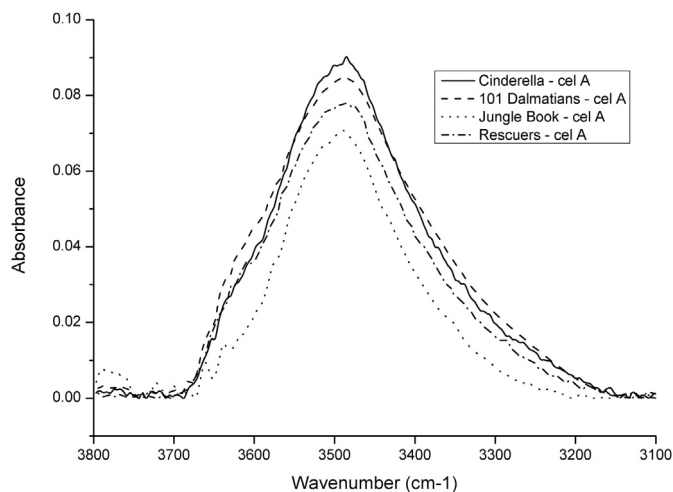
Fig. 6. FTIR spectra of cellulose diacetate (CDA) and cellulose triacetate (CTA) standards. CTA shows a lower and differently shaped O−H stretching band at 3486 cm^{-1} and the shifting of the C=O stretching peak at 1746 cm^{-1}.

Fig. 5, the % acetyl content results of the unplasticized CA animation cels based on GC/MS analysis, shows clusters for CDA (acetyl content between 35 and 41%) and CTA (acetyl content between 43 and 45%). The dashed lines designate the ranges of acetyl content that yielded the optimum workability for CDA plastic sheets, and CTA primary cellulose acetate. It is evident that the acetyl contents of roughly half of the cels fall below these two ranges, meaning that partial hydrolysis may have occurred for these cels. However, because cellulose diacetate is manufactured by partial hydrolysis of cellulose triacetate, the degree of substitution and acetyl content will vary with the time of reaction. Thus, the spread in data may also be due to slight variation in the original acetyl content for individual batches of these commercial plastics.

Fig. 6 shows the comparison between FTIR spectra of CDA and CTA standards. As mentioned previously, different degrees of acetylation lead to different intensities and shapes of the hydroxyl band at 3486 cm^{-1}, and different intensities and positions of the carboxyl peak at 1746 cm^{-1}. Fig. 7 illustrates the intensities of the hydroxyl band of various CDA cels and coversheets, and the correlation between age of the sample and the intensity of the O−H

band is obvious. By plotting the O−H to C=O peak area ratios for the cels versus date of production, two clusters are evident relating to the CDA and CTA polymers (Fig. 8). Looking at the CDA data cluster, there is a slightly increasing trend of deacetylation relating to age which, as mentioned earlier, may be due to partial hydrolysis or to batch variations in manufacturing. Conversely, there is less spread in the data cluster for the CTA cels, and no obvious trend with age. Perhaps because CTA is formed by complete acetylation of α-cellulose, there is less variation in composition during manufacturing, and also the polymer is more resistant to sunlight, temperature and moisture [8].

In order to minimize the effects of production date on the FTIR ratio results, Fig. 9 is a graph of the O−H to C=O ratio versus % acetyl content. The two data clusters relate to the CDA and CTA polymers in the cels. Linear regression fitting to the data gave a correlation of 0.74, which is somewhat disappointing considering that the effects of plasticizer on the polymer analysis results should have been negligible. In light of the accuracy and reproducibility of the GC/MS procedure for measuring acetyl content and the need to extract plasticizers prior to measurement, FTIR offers no particular advantage as a tool for assessing the extent of deacetylation of CA polymers.

Fig. 7. O−H stretching band from FTIR spectra of selected cellulose diacetate animation cels.
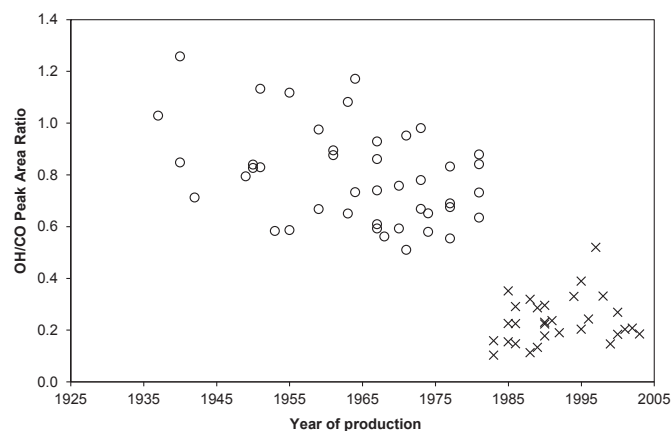
Fig. 8. FTIR results for animation cels showing the O−H to C=O peak area ratio versus year of production for cellulose diacetate (○) and cellulose triacetate (×) cels.
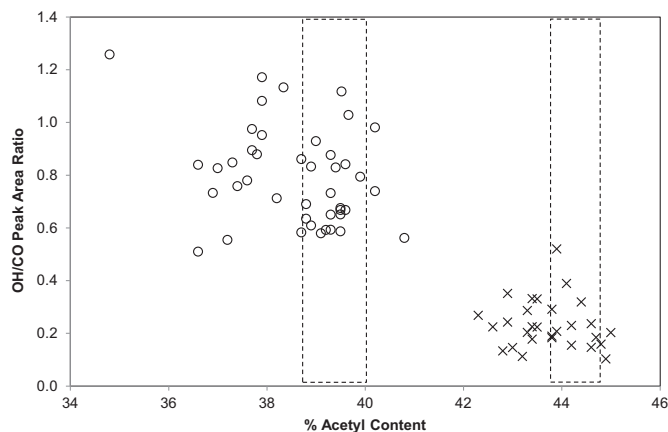
Fig. 9. FTIR peak area ratio versus % acetyl content for cellulose diacetate (○) and cellulose triacetate (×) cels.

4. Conclusions

The results from this study of cellulose acetate animation cels in the collections of the Walt Disney Animation Research Library illustrate the value afforded by invasive test methods for characterizing cels. One of the most important discoveries of the research concerned the inherent variability of the cel compositions in the collection. For example, FTIR showed that between 1981 and 1983 there was a transition from cellulose diacetate to cellulose triacetate as the primary cel material. Additionally, eleven different plasticizer mixtures were identified by Py-GC/MS in the cels. Given this material complexity, it is clear that future experiments to measure cel behavior and response to changing environmental conditions should be conducted on a subset of production cels that represents the range of known compositions, instead of on specimens of commercial cellulose acetate which are limited in the range of available plasticizers.

The solvent extraction procedure for measuring the plasticizer content of cellulose diacetate and cellulose triacetate cels was shown to be more reliable than thermogravimetry, and the residual, highly-purified cellulose acetate polymer could subsequently be analyzed for % acetyl content. The GC/MS method for measuring % acetyl content was shown to be highly accurate, and capable of differentiating CDA and CTA with minimal sample required.

The lack of obvious trends regarding hydrolysis in the % acetyl content of the cels versus production date was consistent with the overall good visual appearance of the cels. In contrast, it is well known that many cellulose acetate sculptures and design art made in the first half of the 20th century cannot be displayed in museums due to degradation and damage, and those remaining on display often have recent repairs. The reasons for this disparity are unknown, but application of the test methods in this study to cellulose acetate art objects may shed some light on this phenomenon.

As future studies of the WDARL cellulose acetate cel collection will focus on optimizing storage conditions to benefit long-term preservation efforts, the results from this analytical survey provide an important point of reference against which the cel compositions can be monitored in relationship to the temperature and relative humidity conditions in the storage environment. It is hoped that this study will, in some way, contribute to preserving this unique cultural legacy.

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