

Physicochemical Studies of Cellulose Acetate Decomposition Reactions*

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Synopsis

This work is a continuation in these laboratories of the study of the source of undesirable optical properties of molded cellulose acetate. The origin, mechanism of formation, and structure of the colored compounds formed upon heating cellulose acetate in the presence of plasticizer were studied. Extraction of heated mixtures gave evidence indicating the colored compounds are intermediates containing a conjugated carbonyl group. Efforts to fractionate and isolate color-causing fractions were defeated by the well-known solvent inclusion difficulties and upset of the little-understood salt balance in the sample. The effects of additives known to degrade cellulose acetate were determined by heating mixtures of these materials with cellulose acetate dissolved in excess plasticizer. Acidic compounds caused the expected severe degradation and color formation. Air oxidation and free radical initiators had very little effect compared to the acidic materials. Inhibitors of the action of acidic compounds (neutralizers) and of oxidative degradation were studied.

Introduction

In previous publications^{1,2} from these laboratories, the effect of particle content on the appearance of molded disks of cellulose esters was discussed. Emphasis was placed on the particles approximately 0.1μ in size which scatter light strongly and limit the maximum clarity of cellulose ester plastics. The present investigation provides some insight into the chemical reactions, particularly degradation occurring during heating of cellulose acetate.

A large amount of literature exists on the chemistry of cellulose acetate degradation, and it would not be possible to review it here in its entirety. A review article by Decroes and Tamblin³ is particularly pertinent and contains many leading references. Evans and McBurney⁴ discussed the stability of cellulose acetate to heat and found the stability to be a function of its ease of oxidation.

Experimental

A series of molded acetate disks (supplied through the courtesy of Mr. L. Kruth, Celanese Polymer Co., Cumberland, Md.) was studied by direct

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transmission measurements over a wavelength range of 350–750 $m\mu$ with a Beckman DK-2 recording spectrophotometer. The composition of the disks was 30 parts diethyl phthalate (DEP) plasticizer by weight per 100 parts of flake. Molding temperature ranged from 180 to 230°C., molding time, from 5 to 60 min., and the molding pressure was 6000 psig. A similar set of disks has been previously studied by Sperling.² Average particle size in the previously studied disks was determined by light scattering, and the numerous small particles present (0.1–0.2 μ diameter) were related to the "haze" in acetone solutions of the cellulose acetate.

In the present investigation the particle diameters were calculated from light transmission data by using a method developed by Doty and Steiner⁵ which assumed monodisperse spheres. The diameter appeared to decrease slowly with molding time (see Table I), but the interference of chemical absorption and other experimental difficulties such as light scattering from uneven surfaces, etc. were significant, and solutions of the disks in acetone were made to alleviate the experimental difficulties.

TABLE I
Particle Diameters in Disks Molded at 190°C. for Varying Times

Molding time, min.	Particle diameter, μ
10	0.187
15	0.196
20	0.190
25	0.184
30	0.154
40	0.145

TABLE II
Change in Optical Density (OD)
after Centrifugation at 90,000G for 15 Min.

Mold- ing time min.	OD at 400 $m\mu$			OD at 500 $m\mu$			OD at 600 $m\mu$		
	Before	After	Δ OD	Before	After	Δ OD	Before	After	Δ OD
10	0.32	0.19	0.13	0.18	0.09	0.09	0.13	0.07	0.06
15	0.29	0.19	0.10	0.17	0.10	0.07	0.12	0.08	0.04
20	0.31	0.20	0.11	0.18	0.11	0.07	0.13	0.08	0.05
25	0.33	0.21	0.12	0.19	0.10	0.09	0.13	0.06	0.07
30	0.34	0.21	0.13	0.19	0.11	0.08	0.13	0.07	0.06
40	0.34	0.22	0.12	0.19	0.11	0.08	0.13	0.08	0.05

The disks which had been molded for different times at 190°C. were dissolved in acetone. These solutions, containing 5% cellulose acetate (CA) by weight, were centrifuged at 90,000G for 15 min. with a Spinco Model L centrifuge. The optical densities were measured before and after centrifuging in cells with a path length of 10 cm., and the change in optical density caused by the centrifugation was determined by difference. The data

are shown for three different wavelengths in Table II. The results show that upon centrifugation at 90,000*G* there is apparently the same decrease in optical density for samples molded for different times and apparently the same amount of haze was present in each original disk molded at various times. The particle size remained very nearly constant and did not decrease with molding time since the plots of log OD (optical density) versus log wavelength are almost linear, with slopes ranging from -1.5 to -2.1 for the different molding times at 190°C.

Extraction of Colored Material from Thermally Degraded Cellulose Acetate

Cellulose acetate was thermally degraded in the presence of air to a dark brown, brittle material. Extractions with various solvents on this dark material were then carried out. Solvents used were water, carbon tetrachloride, hexachloro-1,3-butadiene, methanol, ammonium hydroxide, and pyridine. Ultraviolet and visible spectra of the extract were obtained, and infrared samples were prepared by evaporating to dryness and forming KBr pellets.

The two chlorinated hydrocarbon solvents, carbon tetrachloride and hexachloro-1,3-butadiene, failed to extract any detectable amount of material. Water and methanol extracted colored substituents but did not separate these from cellulose acetate since the infrared pattern of the extracts were identical to those of cellulose acetate. Pyridine extracted more colored material, but this solvent is difficult to handle in making spectroscopic measurements. Concentrated ammonium hydroxide extracted considerable colored material with an infrared spectrum different from that of cellulose acetate. A strong OH band (3.02μ) was evident, but acetate ester bands at 7.80 and 8.15μ were absent. A strong band at 6.00μ was obtained which probably resulted from a conjugated carbonyl, and there was another band at 6.20μ , indicating a carbon-carbon double bond conjugated with a carbonyl. A very small amount of 2,4-dinitrophenylhydrazine derivative was obtained from a solution of cellulose acetate which had been heated in excess diethyl phthalate. The derivative was dark red in color, also suggesting a conjugated carbonyl, but the melting point was not sharp and positive identification was not possible.

Fractionation of Cellulose Acetate

The work of Martin et al.⁷ supports the hypothesis that cellulose acetate will have better thermal stability if certain fractions are removed from the cellulose acetate, and the molded products prepared after fractionation will have higher clarity and lower color. Cotton linters acetate with a degree of substitution (DS) of 2.4 was dissolved in solvent (both acetone and purified dioxane were used), the insoluble haze removed by centrifugation, and the cellulose acetate was reprecipitated with water leaving low molecular weight, soluble products in solution. The haze removed by centrifugation had a slightly higher DS of 2.6 than the original acetate. The supernatant water layer contained less than 1% of the original acetate

and consisted of low DS cellulose acetate, inorganic materials, and colored products with an infrared absorption band of 6.0μ . Molded disks from the purified cellulose acetate had a higher color than the original acetate. This was probably due to the well known fact that thermal stability depends on the washing and drying procedures used on the samples. In this case, washing with distilled water was followed by air drying. The washing probably upsets the critical salt balance in the sample,⁸ and occluded solvent not removed by drying has also caused difficulties.⁹

A more extensive fractionation procedure was run similar to that of Sookne et al.¹⁰ consisting of dissolving the cellulose acetate in acetone and precipitating with 95% ethanol. The cellulose acetate was prepared from cotton linters with low sulfate content and contained no stabilizer. Ethanol was added to the solution at room temperature until it was turbid and the solution was cooled to 5°C . The precipitated acetate formed in the bottom of the container and the supernatant liquid was decanted. A control sample was prepared by reprecipitating as much of the cellulose acetate as possible with ethanol and water. The characteristics of the fractions are summarized in Table III, along with a comparison of the heat stability of fractions with and without excess DEP. The fractions discolored at temperatures lower than the original acetate, probably for the same reasons cited above, upset salt balance and occluded solvent.

TABLE III
Characterization of Acetate Fractions

Fraction	Wt., % of orig.	Ash, %	Sulfate, %	Ash to sulfate ratio	Discoloration temperature, $^{\circ}\text{C}$.	Disk color
Original	—	0.02	0.001	20.0	250-260	
Original (with DEP)					245-250	0.15
Control	98	0.02	0.001	20	255-265	
Control (with DEP)					230-235	0.84
First	20	0.02	0.002	10.0	240-250	
First (with DEP)					210-215	—
Middle	68	0.01	0.003	3.3	235-240	
Middle (with DEP)					215-220	—
Last	2	—	—	—	230-240	
Last (with DEP)					225-230	—

Color formation was much more rapid in the excess plasticizer than for the samples without plasticizer (12 times as fast for the first and middle fractions). It has been reported³ that plasticizers which are susceptible to oxidation induce oxidative degradation in the cellulose acetate. The effects of removing water solubles and of the method of drying (physical structure) on molded disk stability are illustrated in Table IV. Sample B-1 shows the deleterious effect on the disk color of removing water solubles by washing with deionized water. Sample B-2 was dissolved in dioxane, reprecipitated, washed in deionized water, and air-dried. B-3 received the

TABLE IV
Effect of Drying and Removal of Water Solubles on Acetate Stability

Acetate	Treatment	Disk color
B	None	0.13
B-1	Washed with deionized water	0.23
B-2	Dissolved, precipitated, washed, and air-dried	0.94
B-3	Dissolved and freeze-dried	0.58

same treatment as B-2 but was freeze-dried to provide a fluffy, low density product. All of the treatments produced a product of lower stability than the original cellulose acetate.

Addition of Degrading Additives to Cellulose Acetate

The degradative effects of several types of materials such as sulfuric acid, bisulfate, combined sulfate, and ferric ion which can be present in commercial cellulose acetate were studied. The optical density of a 5% solution of cellulose acetate in DEP containing a known amount of additive was measured at 400 m μ after the solution was heated for 4 hr. at 200°C. The color formation from two cotton linters acetates with different amounts of combined sulfate plus additives is shown in Table V, along with data showing the effect of acetyl peroxide and air. The acidic compounds, sulfuric acid, bisulfate, and ferric sulfate, caused the expected large increase in color. The acetyl peroxide was surprisingly ineffective and heating in an air stream caused very little color relative to the acidic materials. The acetate with the higher combined sulfate produced more color than the one with low combined sulfate, as expected.

TABLE V
Effects of Heating Degrading Additives with Cellulose Acetate
at 200°C. in Diethyl Phthalate

Acetate + additive	Additive concentration (based on acetate wt.)	Color (4-hr. OD at 400 m μ) ^a
B + Na ₂ SO ₄ · 10 H ₂ O	120 ppm SO ₄ ⁻	0.12
B, heated under N ₂ stream	—	0.13
B + acetyl peroxide	0.1%	0.14
B, no additive	(Contained 10 ppm SO ₄ ⁻)	0.18
B, heated under air stream	—	0.24
A, no additive	(Contained 220 ppm SO ₄ ⁻)	0.25
B + NaHSO ₄ · H ₂ O	120 ppm SO ₄ ⁻	1.17
B + Fe ₂ (SO ₄) ₃	90 ppm SO ₄ ⁻	1.47
B + conc. H ₂ SO ₄	60 ppm SO ₄ ⁻	2.30
B + conc. H ₂ SO ₄	120 ppm SO ₄ ⁻	3.21

^a After a 1:1 dilution.

Inhibition of Degradation of Cellulose Acetate

Inhibition of degradation of cellulose acetate containing a known amount of sulfuric acid (60 ppm) by a series of compounds of different types was studied. The original acetate contained 10 ppm sulfate, bringing the total to 70 ppm. Compounds used and their classification were as follows: (1) antioxidants (hydroquinone, *tert*-butyl hydroquinone, resorcinol monobenzoate); (2) acid acceptors (4-phenyl-3-thiosemicarbazide, 1,3-diphenyl-2-thiourea, urea); (3) acid reactor (magnesium acetate).

Viscosity and color developed at consecutive time intervals during heating of a 5% solution of the cellulose acetate in DEP at 200°C. were measured. The results are shown in Table VI. Comparisons are made

TABLE VI
Effect of Inhibitors on Degradation
in Sulfuric Acid-Treated Samples of Acetate

Inhibitor	Concentration, wt.-% (based on cellulose acetate)	Effect on degradation	
		Color	Viscosity
Magnesium acetate	0.33	Excellent	Excellent
Urea	0.33	Undetermined	Excellent
Resorcinol monobenzoate	0.33	None	Slightly better
<i>tert</i> -Butyl hydroquinone	0.33	None	Slightly better
Hydroquinone	0.33	None	Slightly better
1,3-Diphenyl-2-thiourea	1.6	Bad	Good
4-Phenyl-3-thiosemicarbazide	0.04	Bad	Bad

with a blank sample without added acid or inhibitor, heated in an identical manner. The acid reactor, magnesium acetate, was the most effective inhibitor of the ones studied. The antioxidants were without apparent effect, particularly on the color formation. The two compounds causing color, 1,3-diphenyl-2-thiourea and 4-phenyl-3-thiosemicarbazide, decomposed under the experimental conditions to produce highly colored materials themselves.

Two of the inhibitors, magnesium acetate and hydroquinone, were examined for ability to prevent color formation and viscosity loss in the original acetate with 10 ppm combined sulfate (no sulfuric acid added). Three concentrations of magnesium acetate were used and the results are shown in Table VII. A large excess of magnesium acetate (3300 ppm) caused con-

siderable color formation. The antioxidant, hydroquinone, prevented a severe loss in viscosity.

TABLE VII
Effect of Inhibitors on Degradation of the Original Acetate

Inhibitor	Concentration wt.-% (based on cellulose acetate)	Effect on degradation	
		Color	Viscosity
Magnesium acetate	33 ppm	Good	Slight improvement
Magnesium acetate	330	Slight improvement	Slight improvement
Magnesium acetate	3300	Bad	Good
Hydroquinone	330	None	Good

Discussion and Conclusions

Spectroscopic examination of solutions of molded disks shows that no change occurs in the size or number of tiny gels (approximately 0.2μ in diameter) with increased molding times. The increase in color of the disks with increased molding time is therefore due to an increase in chemical absorption and not an increase in light scattering. This result was suspected from previous work in these laboratories,² where it was shown that chemical absorption increased its contribution to color and became important as severe molding conditions were employed, but conclusive data on changes in particle sizes and numbers were not then available. Indications from the previous work² were that particle sizes decreased with increased molding time.

Improving the color and viscosity stability of cellulose acetate by extraction of color-forming materials or by fractionation procedures is a difficult process experimentally. Fractions with both high and low degrees of substitution and fractions high in combined sulfate are readily removed, but any beneficial results from these purifications are more than offset by the twin difficulties of upset salt balance and occluded solvent.

Mildly basic materials such as pyridine and concentrated ammonium hydroxide will extract selectively a considerable amount of colored product formed on heating cellulose acetate in the presence of air. These colored compounds contain hydroxyl groups and conjugated carbonyl groups.

A convenient means of studying the thermal decomposition of cellulose acetate (both viscosity loss and color formation) is the heating of solutions of cellulose acetate in diethylphthalate. The plasticizer causes some degradation, but the amount is small compared to that caused by additives such as acidic compounds.

Acidic compounds were found to be highly effective color formation and chain degradation additives, as expected. Degradation by basic compounds (alkaline browning) did not receive study in this work. Oxidative

color formation and chain degradation by air (with and without the free radical source, acetyl peroxide) were much less pronounced than caused by the acidic additives. Inhibitors, such as magnesium acetate, capable of reacting with acidic compounds were the most effective in preventing color formation and viscosity loss.

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Résumé

Ce travail poursuit l'étude entamée dans ce laboratoire concernant l'origine des propriétés optiques indésirables que peut présenter l'acétate de cellulose moulu. Tout d'abord on a étudié l'origine, le mécanisme de formation et la structure des composés colorés formés après chauffage de l'acétate de cellulose en présence de plastifiant. L'extraction des mélanges chauffés montre que les composés colorés sont des intermédiaires contenant un groupement carbonyle conjugué. Les efforts pour fractionner et isoler les fractions responsables de la coloration ont échoué à cause des difficultés bien connues dues à l'inclusion du solvant et à cause de la répartition saline peu connue l'échantillon. Les effets d'additifs connus comme dégradant l'acétate de cellulose ont été déterminés par chauffage des mélanges de ces matériaux avec de l'acétate de cellulose dissous dans un excès de plastifiant. Des composés acides sont la cause de la dégradation considérable observée et de la formation de la couleur. L'oxydation à l'air et les initiateurs à radicaux libres ont un effet faible, comparés aux matériaux acides. On a étudié des inhibiteurs de l'action des composés acides (neutralisants) et de la dégradation oxydante.

Zusammenfassung

Die vorliegende Arbeit bildet eine Fortsetzung der in unseren Laboratorien ausgeführten Untersuchung der Ursache für unerwünschte optische Eigenschaften von Celluloseacetatpresskörpern. Ursprung, Bildungsmechanismus und Struktur der beim Erhitzen von Celluloseacetat in Gegenwart eines Weichmachers gebildeten gefärbten Verbindungen wurden untersucht. Die Extraktion erhitzter Mischungen lieferte Hinweise auf den Charakter der gefärbten Verbindungen als Zwischenprodukte mit einer konjugierten Carbonylgruppe. Fraktionierungsversuche, die zu einer Isolierung der farbbildenden Fraktionen führen sollten, blieben, wegen der wohlbekanntem Schwierigkeiten durch Lösungsmiteileinschluss und der Störung der schlecht bekannten Salzbildung der Probe, ohne Erfolg. Der Einfluss von Zusätzen mit bekannter Abbauwirkung auf Cellu-

loseacetat wurde durch Erhitzen von Mischungen dieser Stoffe mit in überschüssigem Weichmacher gelöstem Celluloseacetat bestimmt. Saure Verbindungen führten zu dem erwarteten, einschneidenden Abbau und zur Farbbildung. Luftoxydation und radikalbildende Stoffe besaßen in Vergleich zu den sauren Stoffen nur eine sehr geringe Wirkung. Inhibitoren für die Wirkung saurer Verbindungen (Neutralisatoren) und für den oxydativen Abbau wurden untersucht.

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