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# MECHANICAL PROPERTIES OF CELLULOSE ACETATE AS RELATED TO MOLECULAR CHAIN LENGTH

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ABSTRACT

The mechanical properties of films prepared from a series of fractions of cellulose acetate, varying widely in molecular chain length (*DP*), were determined. A fraction of *DP* 30 would not form a coherent film; fractions of higher *DP* showed a rapid improvement of mechanical properties with increase in *DP*, but above 150, further improvement was slight. A close correlation was found between the results of folding endurance and ultimate elongation measurements. These properties are more sensitive than tensile strength to changes in *DP* and heterogeneity with respect to *DP*. Investigation of the properties as a function of both weight-average and number-average *DP* indicated that at any given weight-average *DP*, the fractions are superior to the blends and furthermore, those blends which contain fractions of low *DP* are inferior to those which do not. In contrast, at any given number-average *DP* within the range studied, the properties of the fractions and all of the blends are approximately equal.

CONTENTS



## I. INTRODUCTION

The mechanical properties of a cellulosic material are influenced by both the average molecular chain length (*DP*) [2] and the distribution of chain lengths of the molecules of which it is composed. There is

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[2] By *DP* (degree of polymerization) is meant the average number of glucose residues per chain. For linear polymers, such as cellulose and its derivatives, *DP* is a measure of chain length. *DP* will henceforth be designated either $DP_n$, (number-average *DP*) or $DP_w$ (weight-average *DP*). These are more specifically defined as follows:

$$DP_n=\frac{\Sigma n_i DP_i}{\Sigma n_i},$$

and

$$DP_w=\frac{\Sigma w_i DP_i}{\Sigma w_i},$$

where $n_i$ is the number of molecules of *DP*, $DP_i$; and $w_i$ is the total weight of that molecular species [1].

[3] Figures in brackets indicate the literature references at the end of this paper.

general agreement, at least for such linear high polymers, concerning the relationship between the *DP* and some of the mechanical properties of a series of relatively homogeneous fractions. Thus it has been shown that below a certain *DP*, characteristic for each material, no useful filaments or films can be formed. At slightly higher *DP*'s, there is a rapid improvement in the mechanical properties with increase of chain length, whereas at very high *DP*'s these properties are nearly independent of chain length [2, 3, 4].

No such agreement exists, however, concerning the relationship of chain length to mechanical properties when the materials are very heterogeneous. Several investigators have reported that a blended material gives films or filaments with mechanical properties superior to those prepared from a fraction of the same average $DP_w$'s [5, 6, 7, 8]; others have found the blended materials to be inferior [3, 4, 7, 9] or approximately equal in properties [10]. Some of their results are summarized in table 1, which compares the properties of fractions and blends at corresponding $DP_w$'s. In interpreting this table, it should be remembered that the results for films are not necessarily directly comparable with those for filaments, since the degree of orientation is probably considerably greater for the latter in most cases. In addition, the sensitivity of various mechanical properties to changes in homogeneity varies considerably. Unfortunately, most of the investigators have studied only the tensile strength, a property which has been shown to be relatively insensitive to changes in homogeneity [4].

In a previous publication [11], the preparation of a series of samples of fractionated cellulose acetate of widely different $DP_w$'s was described. The present paper reports the results of studies of the effect of chain length and of heterogeneity with respect to chain length on a

TABLE 1.—*Homogeneity and mechanical properties of some high-polymeric materials*

| Material | Mechanical properties investigated | Conclusions | Investigator | Reference |
|---|---|---|---|---|
| Cellulose acetate films | Tensile strength | Blends superior to fractions of corresponding *DP*'s. | Rocha | [5] |
| Cellulose acetate filaments. | do | do | Ohl | [6] |
| Do | do | Materials of low *DP* exert a harmful effect, and those of intermediate *DP* a beneficial effect on the tensile strengths of blends of the same average *DP*. | Mark | [7] |
| Cellulose nitrate films | Load-elongation curve. | In region of plastic flow of load-extension curve, blends require a higher load to produce a given elongation than do fractions of corresponding *DP*'s. | Medvedev | [8] |
| Do | Tensile strength, and ultimate elongation. | Little difference between fractions and blends. | Rogovin and Glazman. | [10] |
| Do | Tensile strength, ultimate elongation, and folding endurance. | Folding endurances of blends inferior to those of fractions of corresponding *DP*'s. Tensile strengths and ultimate elongations insensitive to changes in heterogeneity. | Spurlin | [4] |
| Viscose filaments | Numerous measures of strength and flexibility. | Material of low *DP*'s exerts a disproportionate harmful influence on the mechanical properties of blends. | Schieber | [9] |
| Vinyl chloride-acetate copolymer plastic. | do | Blend inferior in fatigue resistance and approximately equal in strength to fraction of corresponding *DP*. | Douglas and Stoops. | [3] |

number of the mechanical properties of films prepared from these materials and their blends.

## II. EXPERIMENTAL PROCEDURE

### 1. MATERIALS

The cellulose acetate fractions have been described in a previous publication [11]. They varied in $DP_w$, as determined viscometrically, from 30 to 380.

### 2. METHODS

#### (a) PREPARATION OF FILMS

Films 0.0025 to 0.0035 in. thick were prepared as follows: An acetate sample was shaken with a quantity of acetone, sufficient to give a solution with a viscosity of about 400 centipoises, until a homogeneous solution was obtained. The solution was poured onto a glass plate, and spread with a doctor blade, which was held at a predetermined distance above the plate by means of runners. The plate was then placed in a carefully leveled rack. The above operations were performed in a cold room which was maintained at a temperature of approximately 10° C to decrease the rate of evaporation of the acetone. When the film was dry, it was wetted with water, removed from the plate, and then soaked in distilled water at 50° C for 3 hours to remove residual solvent. Films prepared by this method were uniform in thickness to $\pm 0.0003$ in.

#### (b) ESTIMATION OF RELATIVE WEIGHT-AVERAGE CHAIN LENGTH

The $DP_w$'s of the blends were estimated viscometrically in the same manner as was previously used for the fractions [11]. The specific viscosities of dilute solutions of the blends in Methyl Cellosolve (ethylene glycol monomethyl ether) were measured at 25° and 60° C, and Staudinger's relationship [12] was used to calculate the $DP$'s. The $DP$'s reported later are the means of the values obtained at the two temperatures. Because of the limitations of the method of determining them [13], the $DP$ values should be considered as relative values.

#### (c) MEASUREMENT OF MECHANICAL PROPERTIES OF FILMS

All the measurements of the mechanical properties of the films were made in an atmosphere having a relative humidity of 65 percent and a temperature of 21.1° C. Films approximately 0.003 in. thick were used for all of the tests. The actual thickness of each test sample was measured with a dial gage (graduated in ten-thousandths of an inch and with a foot pressure of 4 lb/in$^2$.

The tensile strengths and ultimate elongations of the samples were measured on a "constant-rate-of-elongation" Schopper tensile tester equipped with a recording chart. Samples 0.25 in. wide were used. The distance between the jaws was 3 in., and the rate of separation of the heads was 12 in. per minute when the machine was running free. The minimum thickness of each strip was used in calculating the tensile strengths. At least 10 measurements were made on each fraction and blend. The probable error of the mean for a set of measurements was approximately 3 percent for the tensile strengths and 10 percent for the ultimate elongations.

The folding endurances of the samples were measured by means of an MIT fold tester [14], with a tension of 1.5 kg. Strips 1.50 cm wide were used. Since the folding endurance is fairly sensitive to the thickness of the test strip (thinner films having a higher folding endurance in this range of thickness), it was necessary to correct the results to a standard thickness (0.003 in.) of test strip. This was done by applying small empirical correction factors, which were determined by measuring the folding endurances of strips of the same material but of different thicknesses. The correction factors were determined for several blends of fractions as well as for two commercial cellulose acetates, and were found to agree within 4 percent for a given thickness. About 15 strips were used for the measurement of the folding endurance of each fraction and blend. The probable error of the mean was approximately 8 percent.

Folding-endurance measurements were made both in the direction in which the doctor blade was moved in spreading, and at right angles to this direction. No significant difference was found in the properties in these two directions. This result indicates that, as far as the mechanical properties are concerned, the films do not have "machine" and "cross" directions.

The bursting strengths of the films prepared from the fractions were measured on a Mullen tester [15]. Ten bursts were made for each sample, and the results were corrected to a film thickness of 0.003 in.

## III. RESULTS

### 1. MECHANICAL PROPERTIES OF THE FRACTIONS

The variation of the tensile and bursting strengths of the fractions with $DP_w$ is shown in figure 1. As would be expected, there is a close correspondence between the two properties [15]. The general shape of the curve for the tensile strengths agrees well with the results obtained by other investigators [2, 3], although it is apparent that the strength is by no means independent of chain length in the range of *DP*'s covered by these materials. The material of *DP* 30 would not form a coherent film, and was therefore assigned a strength of zero.

In addition to the above measures of strength, impact-strength measurements were made on thin, narrow strips of the fractions.[4] The shape of the curve obtained by plotting impact strength against $DP_w$ was closely similar to that for the bursting and tensile strengths. It is of interest to note that for all three of the strength tests described above, the starting material (designated by tagged circles in fig. 1) appears to be only slightly, if at all, inferior to a fraction of corresponding $DP_w$.

The ultimate elongations and folding endurances of the fractions are shown in figure 2. The results indicate a close relationship between these two quantities, and as will be shown later (section III–2), a similar correspondence was found for the blends. Both of these mechanical properties appear to be independent of chain length above a $DP_w$ of approximately 150. The original material does not appear to differ significantly from a fraction of corresponding $DP_w$.

The first fraction obtained in the fractional precipitation procedure was characterized by its haziness and high ash content. Because it

[4] We are indebted to F. D. Pilgrim and W. O. Kearse of the Tennessee Eastman Corporation for making the impact-strength measurements.

was not completely soluble in acetone or Methyl Cellosolve, no estimate of its $DP_w$ was obtained, and the data for its mechanical properties are therefore not included in figures 1 and 2. This material had a tensile strength of 1,000 kg/cm$^2$, a folding endurance of 86, and an ultimate elongation of 18 percent. These mechanical properties are similar to those of the fractions of high $DP_w$.

It should be noted that at low $DP_w$'s, the folding endurance is much

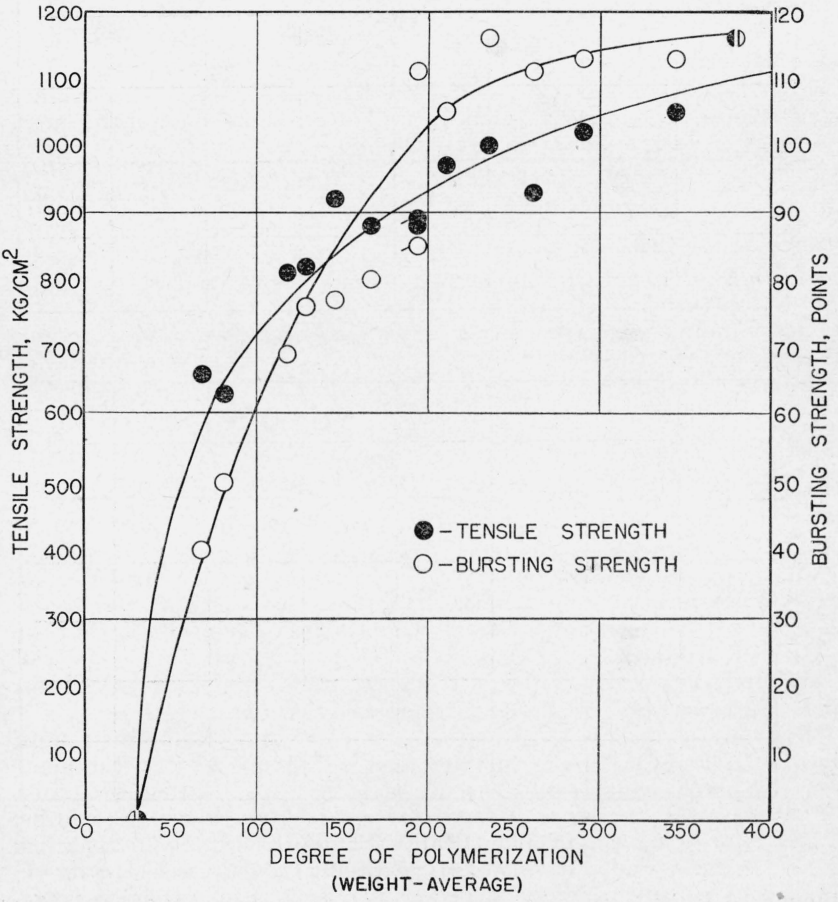


FIGURE 1.—*Tensile and bursting strengths of cellulose acetate fractions as a function of the viscometrically estimated DP.*

The starting material is designated by tagged circles.

more sensitive to variation in chain length than is the tensile strength. The ratio of the highest folding endurance to the lowest (with the exception of the fraction that will not form a film) is about 5:1; the corresponding ratio for the tensile strengths is less than 2:1.

A number of other mechanical properties [5] of the fractions were measured in addition to those described above. They are referred

[5] Measurements have been made of the flow characteristics (elongation as a function of time at constant load) of several of the fractions and the starting material. These results will be presented elsewhere, together with some results of load-elongation measurements on these materials [16].

to only briefly, since they show little variation with chain length. Films prepared from fractions of *DP*'s 67 and 380 were found to have moduli of rigidity which did not differ significantly. The flexural resiliencies, as measured with the Schiefer Flexometer [17], of these

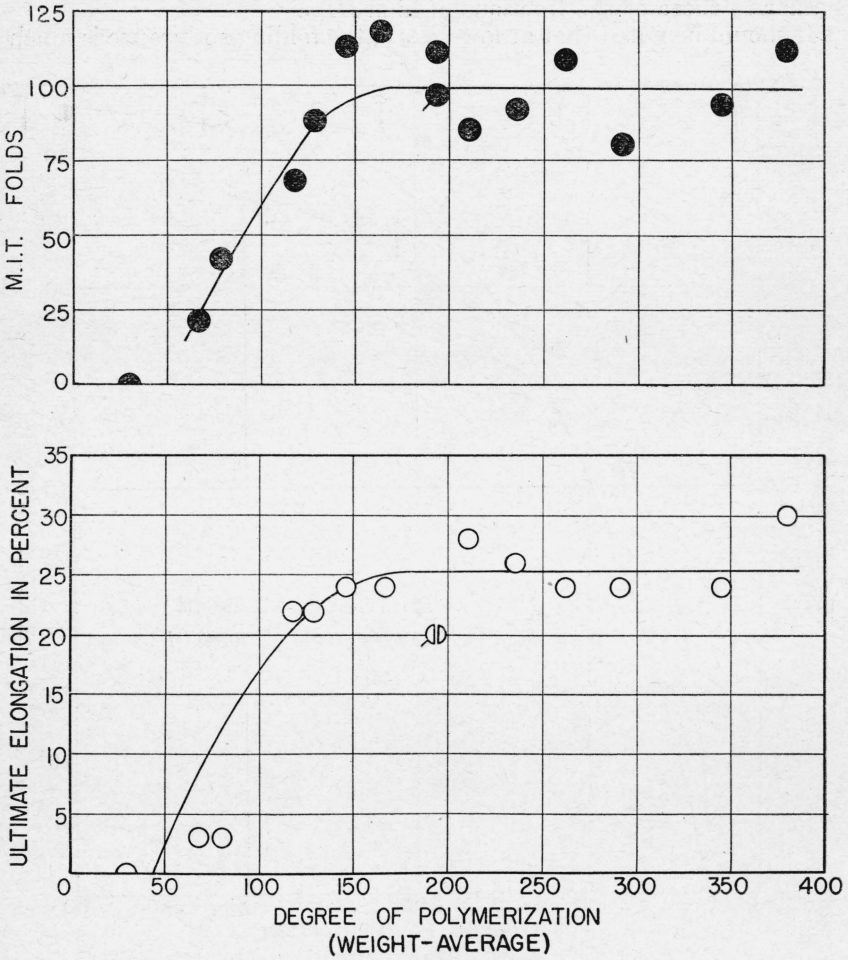


FIGURE 2.—*Ultimate elongations and folding endurances of cellulose acetate fractions as a function of the viscometrically estimated DP.*

The starting material is designated by tagged circles.

two fractions and of the starting material were found to agree within the experimental error.

### 2. MECHANICAL PROPERTIES OF BLENDS OF THE FRACTIONS

In order to study the effect of heterogeneity with respect to molecular chain length on the mechanical properties, a comparison of these properties for blends of different composition was made. The results are given in table 2 and shown graphically in figures 3 to 7.

TABLE 2.—*Properties of blends of cellulose acetate fractions*

| Designation | Composition | Weight percentage of lower *DP* | Weight-average *DP* (calc.) | Weight-average *DP* (obs.) | Number-average *DP* (calc.) | Folding endurance | Tensile strength | Ultimate elongation |
|---|---|---|---|---|---|---|---|---|
| | | | | | | *Folds* | *kg/cm²* | *Percent* |
| 1 [a] | 380+30 | 0 | 380 | 380 | 380 | 112 | 1,160 | 30 |
| A | 380+30 | 5 | 363 | 360 | 240 | 90 | 1,140 | 26 |
| B | 380+30 | 25 | 293 | 281 | 97 | 81 | 900 | 21 |
| C | 380+30 | 51 | 200 | 180 | 55 | 34 | 690 | 10 |
| D | 380+30 | 75 | 118 | 106 | 39 | 10 | 600 | 2 |
| E | 380+30 | 95 | 48 | 47 | 31 | 0 | 0 | 0 |
| 15 [a] | 380+30 | 100 | 30 | 30 | 30 | 0 | 0 | 0 |
| F | 380+81 | 5 | 365 | 369 | 321 | 114 | 1,010 | 19 |
| G | 380+81 | 25 | 305 | 294 | 197 | 134 | 1,050 | 24 |
| H | 380+81 | 60 | 200 | 169 | 118 | 67 | 730 | 9 |
| I | 380+81 | 80 | 141 | 134 | 96 | 75 | 780 | 12 |
| J | 380+81 | 95 | 96 | 99 | 85 | 58 | 730 | 8 |
| 13 [a] | 380+81 | 100 | 81 | 81 | 81 | 42 | 630 | 3 |
| K | 380+167 | 5 | 369 | 370 | 358 | 122 | 1,180 | 31 |
| L | 380+167 | 45 | 284 | 279 | 241 | 130 | 1,000 | 25 |
| M | 380+167 | 84 | 200 | 198 | 184 | 108 | 820 | 18 |
| N | 380+167 | 95 | 178 | 179 | 172 | 132 | 960 | 25 |
| O | 380+167 | 100 | 167 | 167 | 167 | 117 | 880 | 24 |
| P | 380+68 | 58 | 200 | 183 | 104 | 67 | 780 | 10 |
| Q | 380+129 | 50 | 255 | 247 | 193 | 103 | 1,020 | 25 |
| R | 380+129 | 72 | 200 | 196 | 158 | 125 | 780 | 17 |
| S | 291+81 | 43 | 200 | 195 | 138 | 74 | 940 | 24 |

[a] The properties of the fractions of *DP*'s 30, 81, 167, and 380 have been included for comparison. The fractions are numbered to correspond with their designations in a previous paper [11].

Figure 3 shows the tensile strengths of the blends plotted against $DP_w$. The curves for the three series of blends ($DP_w$'s 380+30, 380+81, and 380+167) have been represented by solid lines as a matter of convenience, although the data are such that these curves are somewhat ambiguous. The dotted line, which is traced from figure 1, is the curve for the fractions. The results appear to indicate a small but measurable harmful effect of the shorter chains on the tensile strength, since the results for the blends fall below the dotted line in general, especially for those blends which contain the fraction of $DP_w$ 30.

A similar but much larger effect is shown by measurements of the folding endurance and ultimate elongation (fig. 4). The curves for the series of blends 380+81 and 380+30 are markedly lower than the curves for the fractions (dotted lines, traced from fig. 2). The line for the folding endurances of the series 380+167 is, however, somewhat higher than the corresponding curve for the fractions. While there is a possibility that this may represent a slight superiority of these blends over the fractions, this does not appear too likely, since this effect is not shown by the results of the ultimate elongation measurements.

The effect of the shorter chains on the mechanical properties of blends of different composition, but all of $DP_w$ 200 is shown in figure 5. The values of the mechanical properties for the blends of the pairs 380+30, 380+81, and 380+167 were interpolated from the smooth curves of figures 3 and 4, and the other points represent the values for blends *P* and *Q* of table 2. The graphs clearly demonstrate that the effect of heterogeneity is greater on the folding endurance and ultimate elongation than it is on the tensile strength.

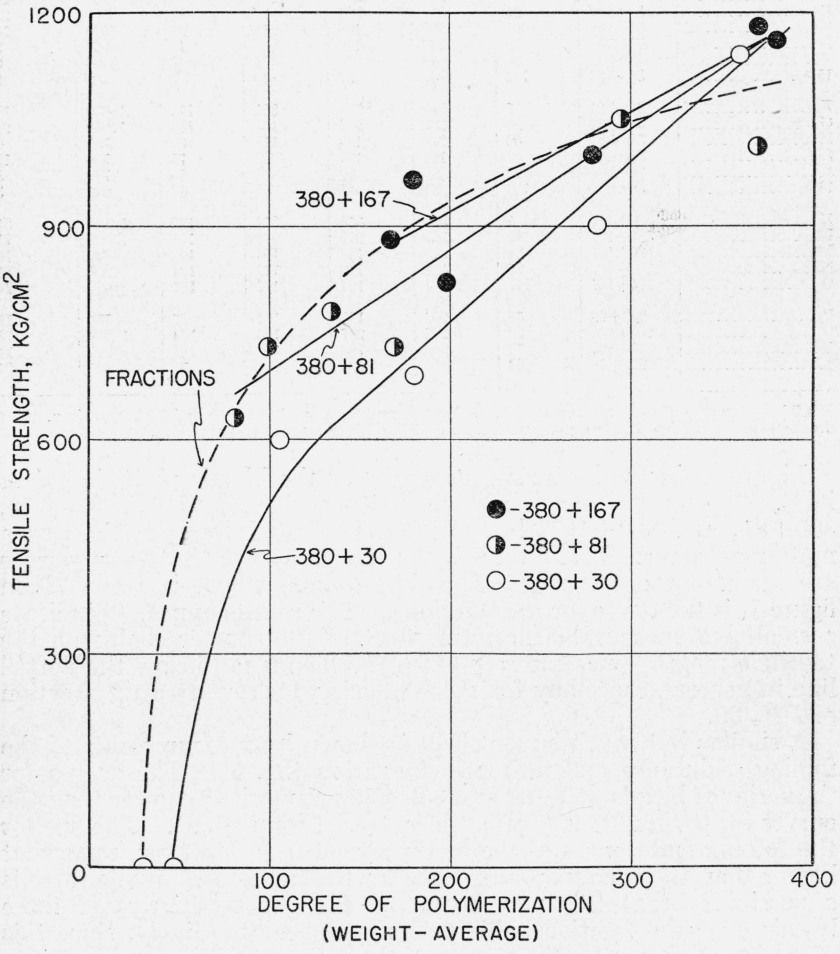


FIGURE 3.—*Tensile strengths of blends of cellulose acetate fractions as a function of the viscometrically estimated (weight-average) DP.*

The dotted line is the curve for the fractions, traced from figure 1. The tagged circle is common to all three series of blends.

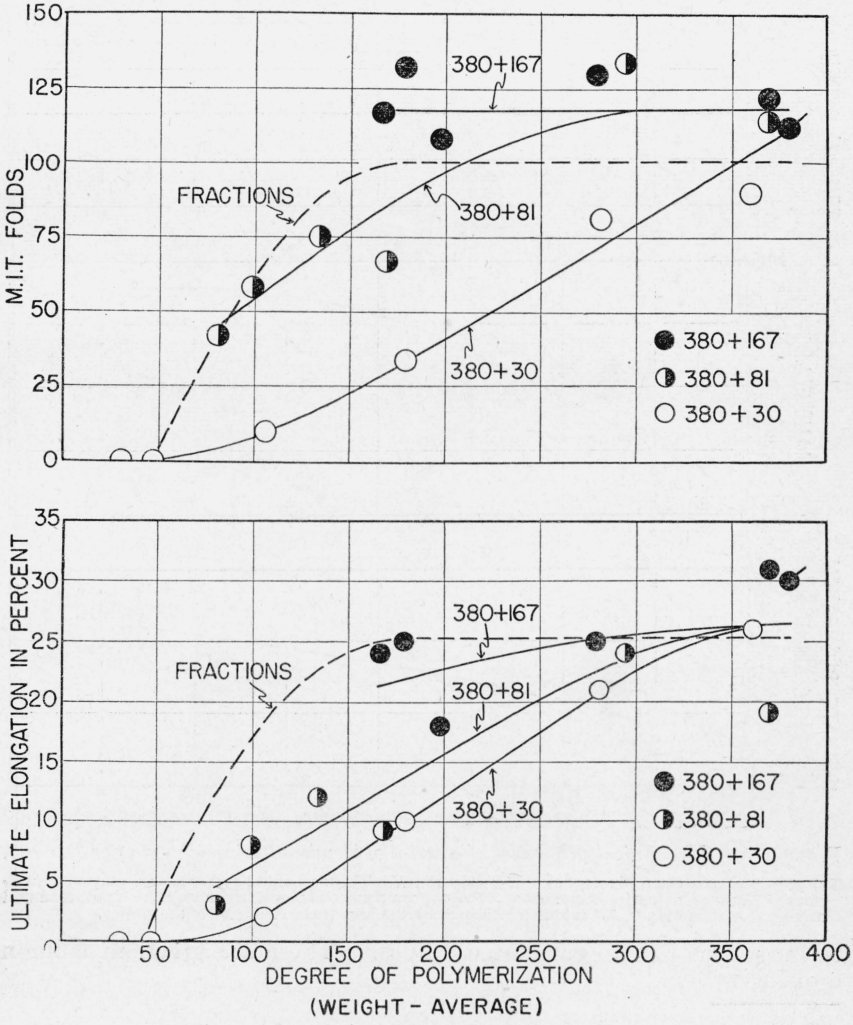


FIGURE 4.—*Ultimate elongations and folding endurances of blends of cellulose acetate fractions as functions of the viscometrically estimated DP.*

The dotted lines are the respective curves for the fractions, traced from figure 2. The tagged circles are common to all three series of blends.

The data presented above indicate that at a given $DP_w$, the materials of shorter chain length exert a harmful effect on the mechanical properties of blends. It is of particular interest to plot the data on the basis of the $DP_n$'s of the fractions and blends as well. This requires the estimation of the $DP$ by other means (such as osmotic pressure measurements) but since such data were not available,[6]

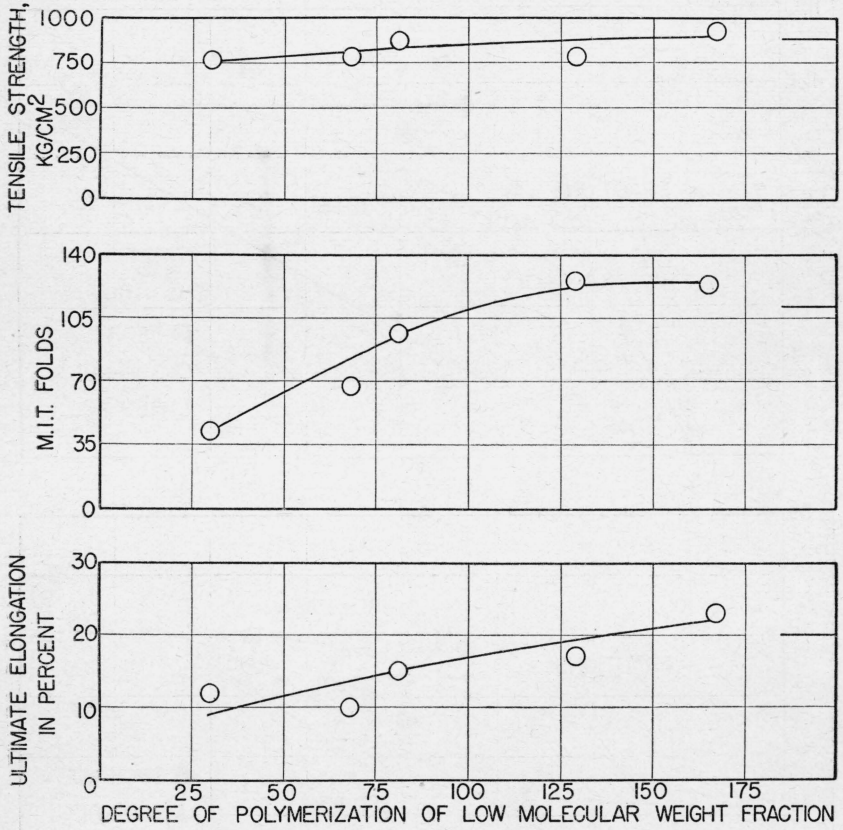


FIGURE 5.—*Mechanical properties of a series of blends, all of weight-average DP 200.*

The blends are composed of fractions of $DP$'s 380 and $X$. The mechanical properties are plotted as functions of $X$, the viscometrically estimated $DP$ of the component of shorter chain length. The mechanical properties of a fraction of $DP$ 194 are represented by the bars at the right side of the graphs.

recourse was had to calculated values.[7] These are given in column 6 of table 2.

[6] Measurements in progress.

[7] The values of $DP_n$ for the blends can be calculated from the formula

$$DP_n = \frac{100}{\frac{f_1 r_1}{DP_{w_1}} + \frac{f_2 r_2}{DP_{w_2}}},$$

where $DP_n$ is the number-average $DP$ of the blend, $f_1$ and $f_2$ are the weight percentages in the blend of the fractions of $DP_{w_1}$ and $DP_{w_2}$, respectively, $r_1 = DP_{w_1}/DP_{n_1}$ and $r_2 = DP_{w_2}/DP_{n_2}$. Since the fractionation process produces fractions that are relatively homogeneous, $r_1$ may be taken equal to $r_2$. The formula given above then reduces to the following:

$$DP_n = \frac{100}{r_1\left(\frac{f_1}{DP_{w_1}} + \frac{f_2}{DP_{w_2}}\right)}.$$

The figures given in column 6 of table 2 were calculated from this formula, with a value of unity assigned to $r_1$. They therefore represent relative calculated values.

The mechanical properties of the blends are plotted against their calculated relative $DP_n$'s in figures 6 and 7. The dotted lines are not drawn to fit the points but are the curves for the respective mechanical properties of the fractions, traced from figures 1 and 2. As shown in figure 6, all of the tensil-strength data for the blends, regardless of composition, are reasonably well represented by the curve for the fractions, although the data for the series of blends

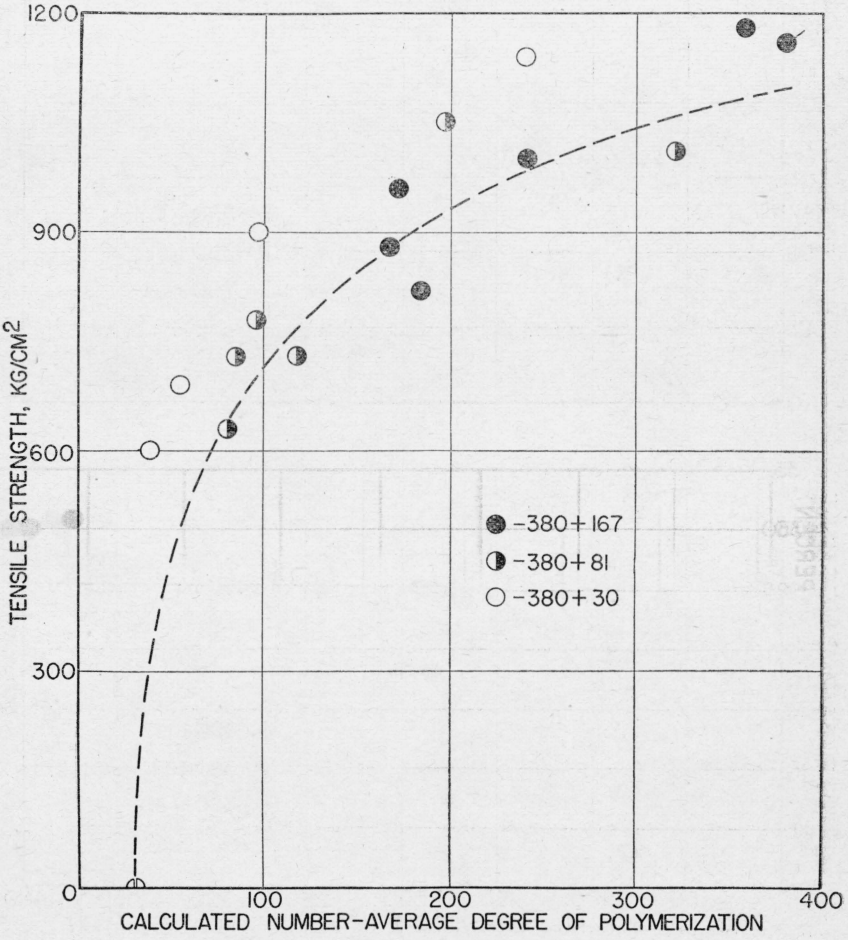


FIGURE 6.—*Tensile strengths of blends of cellulose acetate fractions as a function of the calculated number-average DP.*

The dotted line is the curve for the fractions, traced from figure 1. The tagged circle is common to all three series of blends.

380+30 (open circles, fig. 6) appear to be overcorrected by this method of calculation. Thus, in figure 6 the open circles fall above the dotted line in general, whereas in figure 3 (in which the tensile strengths are plotted against $DP_w$), they fall below it. A more critical test is provided by the folding-endurance data, since the differences caused by the admixture of material of short chain length

are apparently larger for this property. Figure 7 shows that the folding-endurance data for the blends are also reasonably well represented by the curve for the fractions (dotted line). The results for the ultimate elongations appear to parallel the results for the folding-endurance measurements. Figure 7 should be compared

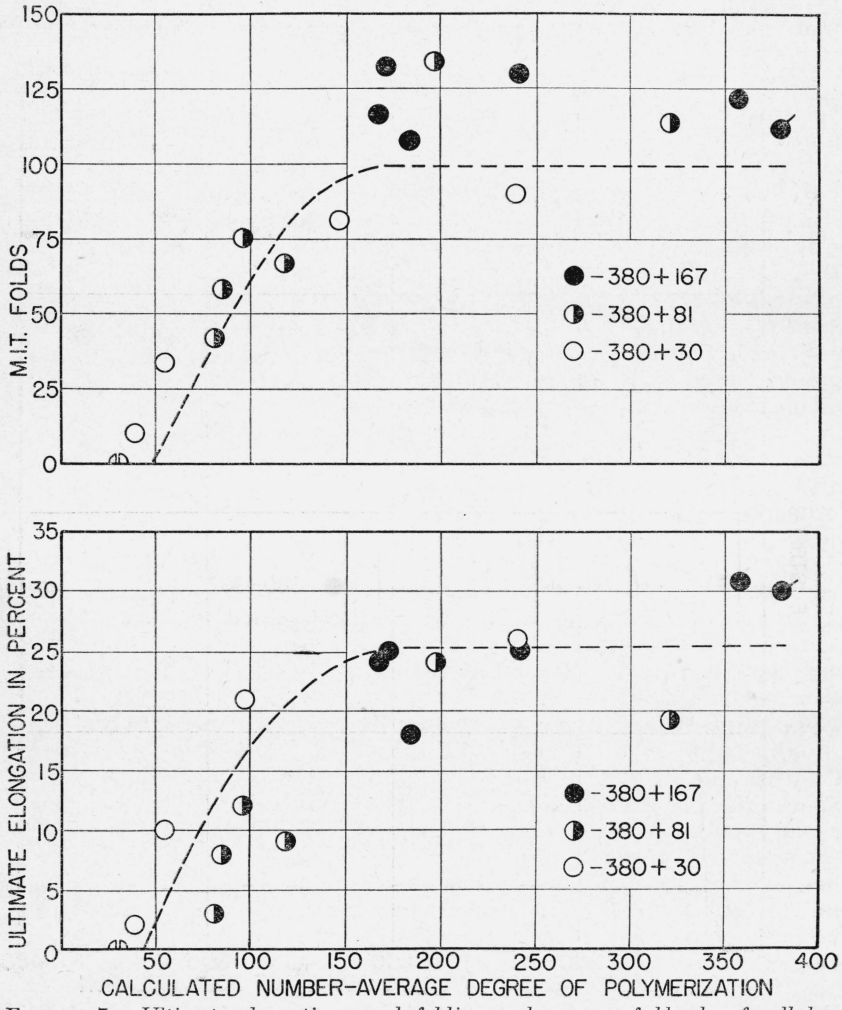


FIGURE 7.—*Ultimate elongations and folding endurances of blends of cellulose acetate fractions as functions of the calculated number-average DP.*

The dotted lines are the respective curves for the fractions, traced from figure 2. The tagged circle is common to all three series of blends.

with figure 4, in which the folding endurances and ultimate elongations are plotted against $DP_w$.

It is of interest to note that the results for the blends P, Q, R, and S (which have not been included in the curves) would also fall close to the dotted lines of figures 6 and 7.

## IV. DISCUSSION

The data described above indicate that when the mechanical properties of the blends are plotted against their $DP_w$'s, a harmful influence of the materials of shorter chain length (approximately $DP_w$ 80 or less) can be observed. The magnitude of this influence is a function of the amount and *DP* of the shorter chains in a blend. On the other hand, the addition of a material of intermediate chain length to one of high *DP* does not appear to produce any marked beneficial or harmful effect. It may thus be said that under the conditions of these experiments, the mechanical properties are monotonic, but not single-valued functions of $DP_w$. On the other hand, when the mechanical properties of the blends are plotted against their calculated $DP_n$'s, all of the data are reasonably well described by a single curve for each property. Since this curve approximates the curve for the fractions, it appears that the mechanical properties of the cellulose acetate films may be described as monotonic, single-valued functions of $DP_n$. In the absence of actual determinations of $DP_n$, this must be regarded as only a tentative hypothesis. It is interesting to note, however, that this hypothesis is qualitatively consistent with the concept that a sample ruptures in the tensile- or folding-endurance tester when a sufficient number of chain ends exist close together in the test strip [18]. This follows, since the number of chain ends in a cross-sectional element of the sample is inversely proportional to $DP_n$. It should be further noted, however, that the range of *DP*'s covered by these experiments is not very large. It is quite likely that the empirical generalization advanced above would not describe the results adequately if materials of very high and very low *DP*'s were blended. The results suggest, however, that for many industrial products, and particularly where materials of high and low *DP*'s are blended, considerable advantage would attach to the determination of $DP_n$, since this quantity appears to be more closely related to the mechanical properties than $DP_w$.

The results described above are consistent with those obtained by a number of other investigators [3, 4, 9]. Since the results of Spurlin [4] on the mechanical properties of nitrate films were obtained under experimental conditions rather similar to those described above, they are of especial interest here. Spurlin found that at corresponding $DP_w$'s, films prepared from fractions were superior in folding endurance to those prepared from straight-run commercial nitrocellulose, and that the latter were in turn superior to blends of the straight-run material. The differences in properties were attributed to differences in homogeneity, and in particular it was concluded that a reasonably smooth distribution curve is desirable in order to obtain good folding endurance. While this is an entirely reasonable deduction for the materials that were being investigated, the results of the present investigation indicate that consideration of the $DP_n$'s of the blends and fractions might have led to a somewhat different interpretation of the results. Unfortunately, since Spurlin's blends were not prepared from fractions, it is impossible to calculate even approximate relative values of the $DP_n$'s for his samples. The data are, however, at least qualitatively consistent with the hypothesis that has been presented above.

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WASHINGTON, November 27, 1942.