

Novel High-Performance Materials from Starch. 3. Influence of Degree of Substitution and Amylose/Amylopectin Ratio on Performance

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The improvements in mechanical properties obtained by orienting starch–ether films were further examined, specifically with regard to their dependence on degree of substitution of the starch and on its amylose/amylopectin ratio. It was found that the degree of substitution had little or no influence on the mechanical properties of these materials at comparable deformations during drying. On the other hand, there were clear dependences of the tensile strength and toughness on the amylose/amylopectin ratio. In particular, the larger this ratio, the stronger and tougher the materials were after orientation. In overall performance, the oriented starch–ether films can be described as tough plastics, with tensile strengths between 15 and 47 MPa, tensile moduli between 320 and 670 MPa, and elongations at break between 5 and 120%. These values are comparable to those of medium-density or even high-density polyethylene.

Introduction

Biodegradable polymers are now extensively used in biomedical applications such as sutures, surgical implants, and controlled-release formulations for drugs.^{1,2} More recently, however, there have been intensive efforts to use these materials in packaging applications.^{2–4} This gives rise to an important challenge in the design of useful polymeric materials that are biodegradable, specifically obtaining an acceptable balance between performance (mainly mechanical properties), biodegradability, and cost. Unfortunately, these three parameters are often mutually exclusive to some extent.^{3,4}

Generally speaking, the detailed chemical structure of a polymer determines whether it is biodegradable, and its morphology determines the rate of biodegradation.^{1–3} These structural effects involve both substituents and chain backbones, and the properties and characteristics include hydrophilicity, stereochemical features, flexibility, and hydrolyzability (particularly that of the chain backbone).² The effects of substituents on the biodegradability of a polymer depend on the type,

their concentrations, and their positionings along the chain backbones. Increasing the concentration of hydroxyl groups in a polymer, for example, tends to significantly increase its biodegradability. A specific example is the addition of hydroxyl substituents to nylons, which is known to increase their susceptibility to fungal attack.⁵ On the other hand, the replacement of hydroxyl groups by other groups usually increases microbial resistance. The best example of this effect involves cellulose; many of its derivatives, such as cellulose nitrates or acetates, have biodegradabilities much smaller than unmodified cellulose itself.⁶ It has also been reported that certain synthetic polymers containing both hydrophilic and hydrophobic segments have better biodegradability than polymers containing only either hydrophilic or hydrophobic segments.^{2,7} This is because in all-hydrophilic systems, strong hydrogen-bond interactions limit the access of otherwise-effective enzymes.⁷ Conformation effects can also greatly influence biodegradability, since high flexibility for example allows a polymer to change conformations so as to be better accommodated into the active site of an enzyme.¹

Recent studies indicated that cellulose acetate could be mineralized if the degree of substitution was ≤ 2.5 (equivalent to ≤ 2.5 substitutions/glucose moiety).^{8,9} This

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Table 1. Orientation Conditions for Triethylamylose Networks with Different Degrees of Substitution

amylose source	maximum swelling ratio ($1/v_{2m}$) ^a	polymer soluble fraction (%)	polym concn at stretching (v_2) ^b
amylomaize VII 75%, DS, air-dried	11–12	5–6	0.2–0.25
amylomaize VII 65%, DS, air-dried	10–12	6–7	0.2–0.25

^a The maximum swelling ratio was measured in chloroform and is a volume ratio. ^b The polymer concentration at stretching was measured in chloroform and is a volume ratio.

illustrates the requirement that there be some free hydroxyl groups for interaction with water and enzymes in order for biodegradation to be initiated. Starch differs from cellulose in two major ways: the glucose rings are joined through carbons 1 and 4 by α rather than β linkages, and considerable chain branching occurs through carbon 6. It is believed that the α linkages in starch are more susceptible to enzyme attack than the β linkages in cellulose. Starch contains two polysaccharides: amylose [α -(1,4)-linked glucose] and amylopectin [α -(1,4)-linked glucose main chains with α -(1,6)-linked branches of α -(1,4)-linked glucose]. The amylose/amylopectin ratio directly affects both the properties and cost of the starch.

Starch is of course directly obtainable from plants. Corn is the primary source for it, although potato, wheat, and rice starches also have markets in Europe, the Orient, and the USA. Most cereal and tuber starches contain approximately 30% amylose, although genetic modifications of corn through agricultural breeding have produced starch with virtually no amylose, called "waxy maize", or with up to 70% amylose ("high-amylose starch"). One major source for the present study was amylomaize VII, a special high-amylose starch produced by American Maize Co. and consisted of approximately 70% amylose and 30% amylopectin. The amylose/amylopectin ratio significantly affects the bulk price of the starch. For standard types of starch (from corn, wheat, rice, and potato) the cost is about \$0.15/lb.³ Higher-amylose starch such as amylomaize VII and amylomaize V (which contains 50% amylose) are somewhat more expensive. Pure amylose is not available commercially in bulk; only laboratory-scale amounts exist, and they are extremely expensive.

Some of these structural characteristics of starch are the focus of this final part of the three-part study. It specifically addresses the influence of degree of substitution and amylose/amylopectin ratio on the mechanical properties of oriented starch-ether films. Also of interest are possible effects of the method chosen to remove the solvent from the swollen networks. The primary purpose was to obtain correlations useful in identifying the best balances among performance, biodegradability, and cost of these oriented starch-based materials.

Experimental Details

Information on "General Methods and Materials",^{10,11} "Hexamethylene Diisocyanate Cross-Linking", "Determina-

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tions of the Soluble Polymer Fractions and Extents of Equilibrium Swelling", "Orientation Procedures", and "Mechanical Property Measurements" are all described in the first two papers in this series.

Since cost directly affects the commercial potentials of these oriented materials, the influence of amylose/amylopectin on performance was one of the primary concerns in this part of the investigation. Six additional types of TEA or triethylstarch (TES) networks were therefore prepared using the amylose V (50% amylose), pure amylose (essentially free of amylopectin), corn starch (30% amylose), rice starch (28% amylose), and wheat starch (21% amylose), respectively. A particular potato starch-ether¹⁰ was synthesized from soluble potato starch. Apparently this starch had a very low molecular weight, and its triethyl ether had very poor film-forming capability. It was therefore not investigated further in this part of the study. In addition, amylopectin-triethyl ether networks were prepared using the same diisocyanate curing process, for purposes of comparison. For the sake of simplifying discussions, all of the materials containing 50% or more amylose were designated triethylamylose (TEA); otherwise, they were designated triethylstarch (TES).

Cross-linked films prepared from these polymers were oriented in a manner similar to that for the TEA (amylomaize VII) gels. A polymer concentration of approximately 0.2–0.25 was used for all six TEA and TES networks, as well as some triethylamylopectin (TEAp) networks.

Results and Discussion

Influence of Degree of Substitution on Mechanical Properties. To enhance biodegradability, the present networks were prepared from triethylamylose (amylomaize VII) having lower extents of substitution. As expected, their water dispersibility increased with the increased hydrophilicity resulting from the low extents of substitution. This would definitely be advantageous for biodegradation. The properties of the triethylamylose and the concentrations used during the stretching procedure are summarized in Table 1. It is interesting to note from these results, and others, that despite substantial differences in degree of substitution, all the TEA (amylomaize VII) gels acquired a similar cross-linking density (as gauged by their maximum swelling ratios in chloroform). These gels had relatively low soluble polymer fractions, ranging from 5 to 9 wt %.

For triethylamylose (amylomaize VII) with a degree of substitution of 75%, both tensile strengths and moduli increased in a manner similar to those having a 90% DS. A 3.2-fold increase in tensile strength and a 100% increase in modulus were observed for films dried at an extension ratio of 135%. They also showed a 45-fold increase in toughness and an approximately 10-fold increase in elongation at break. In addition, at higher stretching ratios during drying, the stress-strain curves of the 75% DS material exhibited yield points, and the yield stress increased from 25.29 to 27.76 MPa, for extension ratios of 100 and 135%, respectively. Again, this observation suggested a higher level of ordering was achieved in highly stretched samples, similar to what

Table 2. Mechanical Properties of Oriented Triethylamylose Films with Different Degrees of Substitution

degree of substitution and (type of deformation)	extension ratio during drying (%)	yield strength (MPa)	elongation at yield (%)	strength (MPa)	elongation at break (%)	tensile modulus (MPa)	toughness (MPa)
90% DS (uniaxial)	0			7.33	3.7	358	0.24
	65	15.55	8.9	14.60	14.0	373	1.75
	100	22.43	10.5	21.27	47.0	423	9.37
	135	24.35	12.2	25.10	106.0	478	24.04
90% DS (biaxial)	30			19.46	11.7	357	1.62
	50			26.12	10.6	418	1.98
	70			30.64	15.5	510	3.69
75% DS (uniaxial)	0			8.10	4.8	206	0.24
	65			17.24	7.7	310	0.86
	100	25.29	16.6	22.22	30.4	376	6.02
	135	27.76	12.4	25.59	45.2	437	10.93
65% DS (uniaxial)	0			8.65	5.7	221	0.35
	65			18.76	9.3	326	1.29
	100	25.28	15.1	23.54	43.5	377	9.23
	135	27.30	15.5	26.91	118.3	413	29.28

was found in the TEA (amylo maize VII) films with a degree of substitution of 90%.¹² Useful ranges of tensile strengths (17.24–25.59 MPa), moduli (310–437 MPa), and elongations at break (7.7–45.2%) were obtained, and these values were comparable to those obtained on TEA (amylo maize VII, 90%).¹² It seemed that a significant reduction in degree of substitution did not affect the final performance characteristics of these oriented films.

Similar improvements in mechanical properties were obtained for oriented TEA (amylo maize VII) films with a degree of substitution of 65%. Both tensile strengths and moduli increased with increase in extension ratio during drying from 0 to 135%. Furthermore, a 65% DS specimen dried at an extension ratio of 135% showed a 3.1-fold increase in tensile strength, an 85% increase in modulus, an 80-fold increase in toughness, and a 20-fold increase in elongation at break. As was the case for oriented TEA films with higher degrees of substitution (75 and 90% DS), higher stretching ratios applied to the TEA 65% DS specimens gave rise to yield points. Also, the yield stress increased from 25.28 to 27.30 MPa, for extension ratios during drying of 100 and 135%, respectively. The oriented 65% DS TEA exhibited ranges of tensile strengths from 18.76 to 26.91 MPa, tensile moduli from 326 to 413 MPa, and elongations at break from 9.3 to 118.3%. These values are comparable to those of the other two TEA (amylo maize VII) materials.

An interesting observation was made concerning the mechanical behavior of the oriented TEA (amylo maize VII) films described in Table 2. For cross-linked but unoriented samples, the tensile strength increased with decrease in degree of substitution (7.30, 8.10, and 8.65 MPa for 90, 75, and 65% DS, respectively). For their oriented analogues, values of the tensile strength were also found to increase slightly with decrease in degree of substitution (25.10, 25.93, and 26.91 MPa for 90, 75, and 65% DS, respectively). The slight increase could

be explained by the increased number of free hydroxyl groups on the polymer backbone, which would enhance the hydrogen bonding in both the oriented and unoriented materials, although these differences were quite small. Increase in extension ratio during drying was a much more important parameter for increasing improvements in mechanical properties.

As illustrated in Table 2, the overall performance of the uniaxially oriented TEA (amylo maize VII) films were relatively insensitive to degree of substitution at similar extension ratios during drying. This information is critical with regard to possible commercialization of such amylose–ether films. Since a lower degree of substitution gives larger numbers of free hydroxyl groups, this insensitivity will make it possible to produce relatively robust materials of high biodegradability. Thus, the results suggest that performance does not necessarily have to be a tradeoff for biodegradability, at least for these oriented triethylamylose materials.

Influence of Amylose/Amylopectin Ratios on Mechanical Properties. As was the case for the TEA (amylo maize VII) networks, these amylose–ether, (starch)–ether networks were found to have relatively low cross-link densities (indicated by their large equilibrium swelling ratios) and relatively low soluble polymer fractions. These results are presented in Table 3.

For oriented TEA (amylo maize V, 80% DS), tensile strengths and moduli were both found to increase monotonically with increase in extension ratio during drying (from 0 to 135%), which is similar to what was observed for TEA (amylo maize VII, 90% DS). More than a 3-fold increase in tensile strength and a 65% increase in modulus were observed at an extension ratio of 135%, as is shown in Figure 1. The stress–strain curves in Figure 2 also exhibited significant increases in toughness and elongation at break with increase in extension ratio during drying. For example, a 15-fold increase in elongation at break and an 80-fold increase in toughness were obtained at an extension ratio of 135%. It was remarkable that although the amylose amount decreased from 70 to 50% in these TEA (amylo maize V) films relative to TEA (amylo maize VII), the improvements in mechanical properties were quite similar. Furthermore, with increase in extension ratio, the yield points in the stress–strain curves became more distinct, and the yield stress increased. For a TEA

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Table 3. Orientation Conditions for Triethylstarch (Triethylamylose) Networks with Various Amylose/Amylopectin Ratios

amylose source	maximum swelling ratio ($1/v_{2m}$) ^a	sol fraction (%)	polym concn at stretching (v_2) ^b
amylomaize V, 80% DS	8–9	7–8	0.2–0.25
amylose (pure), 70% DS	11–12	7–8	0.15–0.25
corn starch, 80% DS	9–10	5–6	0.2–0.25
wheat starch, 80% DS	9–10	9–10	0.2–0.30
rice starch, 80% DS	7–8	6–7	0.2–0.25
amylopectin, 80% DS	8–9	10–12	0.2–0.25

^a The maximum swelling ratio was measured in chloroform and is a volume ratio. ^b The polymer concentration at stretching was measured in chloroform and is a volume ratio.

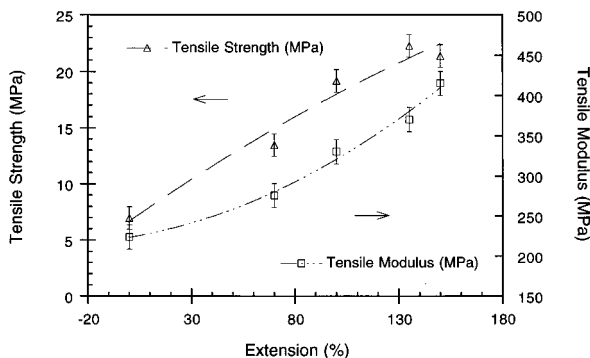


Figure 1. Tensile strength (Δ) and modulus (\square) as a function of extension ratio during drying for uniaxially oriented films prepared from TEA (amylomaize V, 80% DS, air-dried).

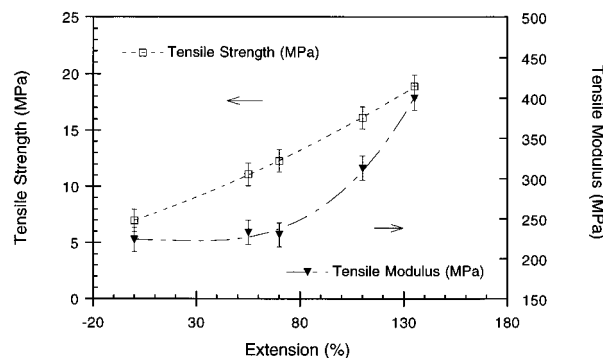


Figure 3. Tensile strength (\square) and modulus (\blacktriangledown) as a function of extension ratio during solvent removal for uniaxially oriented films prepared from TEA (amylomaize V, 80% DS, coagulated).

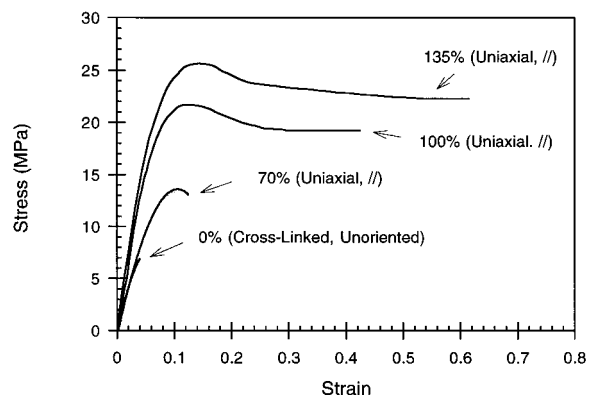


Figure 2. Stress–strain behavior of uniaxially oriented films prepared from TEA (amylomaize V, 80% DS, air-dried).

(amylomaize V) specimen with an extension ratio during drying of 70%, material failure occurred just beyond the yield point (at a stress of approximately 13.49 MPa). With increase in extension ratio from 100 to 135%, the yield stress also increased from 21.71 to 25.65 MPa. All these oriented TEA (amylomaize V, 80% DS) films exhibited useful ranges of tensile strengths (13.31–22.30 MPa), moduli (276–371 MPa), and elongations at break (12.4–61.6%). These values are comparable to those of medium-density to high-density polyethylene.

Results Obtained Using Coagulation for Solvent Removal. Also of interest were possible effects of the process used to remove the solvent from the deformed swollen gels. Preliminary experiments on the TEA (amylomaize VII, 85% DS) films indicated that solvent removal by coagulation usually required less time than air-drying. The results obtained on more controlled solvent-removal experiments on the same TEA (amylomaize V) gels are now described. The degree of substitution, swelling solvent, and polymer concentration at stretching were kept the same, and these

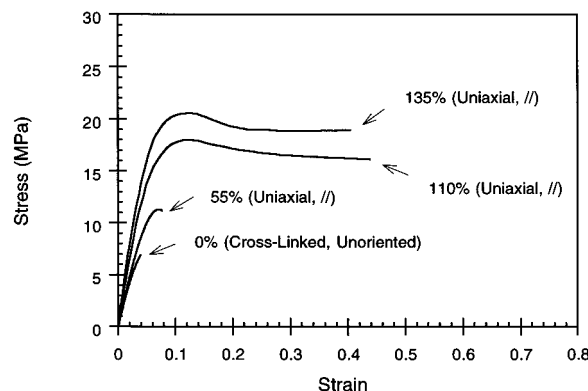


Figure 4. Stress–strain behavior of uniaxially oriented films prepared from TEA (amylomaize V, 80% DS, coagulated).

specimens were deformed uniaxially in the usual manner. At the final stage, however, the chloroform solvent was removed by coagulation in petroleum ether. Some of the mechanical properties of these coagulation-processed samples are presented in Figures 3 and 4. As was the case for the air-dried analogues, tensile strengths, moduli, and toughness all increased monotonically, and frequently dramatically, with increase in extension ratio during drying, over the range 0–135%. A 2.5-fold increase in tensile strength, a 40% increase in tensile modulus, and a 40-fold increase in toughness were observed at an extension ratio of 135%. The samples finished by the coagulation process exhibited tensile strengths ranging from 11.14 to 18.95 MPa, moduli ranging from 233 to 400 MPa, and elongations at break ranging from 7.7 to 43.8%. These values were slightly lower than the values obtained on the corresponding air-dried samples. The differences were possibly due microprecipitations during the relatively rapid coagulation process, since this would disturb the long-

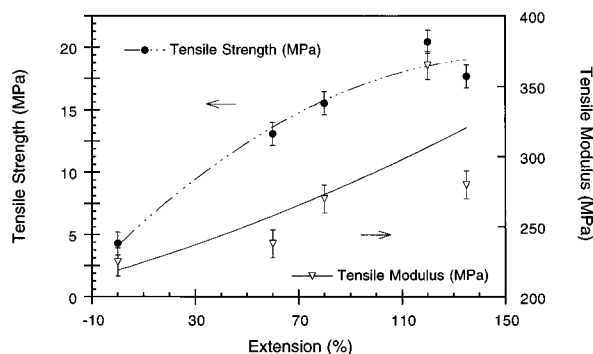


Figure 5. Tensile strength (●) and modulus (▽) as a function of extension ratio during drying for uniaxially oriented films prepared from TES (corn, 80% DS, air-dried).

range ordering in the films. It is worth mentioning that the differences between the oriented TEA (amylo maize V) films finished by the two solvent-removal procedures were found to be somewhat smaller than those for the TEA (amylo maize VII) films.¹²

Results Obtained Using Pure Amylose. For triethylamylose synthesized from pure amylose (70% DS), tensile strengths and moduli were again found to increase with increase in extension ratio during drying. A 3.4-fold increase in tensile strength, an almost 200% increase in modulus, and a 90-fold increase in toughness were obtained at an extension ratio during drying of 140%. At higher stretching ratios, these oriented TEA (pure) films became even tougher, as indicated by a dramatic increase in elongation at break. The stress-strain curves exhibited yield points and the yield stress increased from 37.74 to 49.00 MPa when the extension ratio during drying was increased from 100 to 140%.

The improvements described are similar to those obtained for oriented TEA (amylo maize VII) and TEA (amylo maize V). The only difference was the observation that the absolute values of the mechanical properties were much higher for these oriented TEA (pure) films. Specifically, very high ranges of tensile strengths (21.95–46.95 MPa), moduli (432–670 MPa), and elongations at break (8.9–106.2%) were obtained. The resulting oriented films were almost twice as strong as the films prepared from TEA with lower amylose contents. This was attributed to the complete absence of the highly branched amylopectin.

Although the oriented TEA (pure) films exhibited excellent mechanical properties, their commercial potential would probably be limited by the high cost of pure amylose.

Results Obtained Using Other Types of Starch. Three other types of starch-ethers were employed to investigate their mechanical properties as well as to explore their commercial potentials. These three types of TES networks (from corn, wheat, and rice) were limited to slightly lower maximum extensibilities (ranging from 110 to 120%) than the three types of TEA networks already described. These new types were amylo maize VII, amylo maize V, and pure amylose, at polymer volume fractions of 0.2–0.25 and extensions during drying of 135–150%. The differences observed might be due to the considerably larger amylopectin contents of these starches.

Figures 5 and 6 give the results obtained using TES (corn, 80% DS). The mechanical properties increased

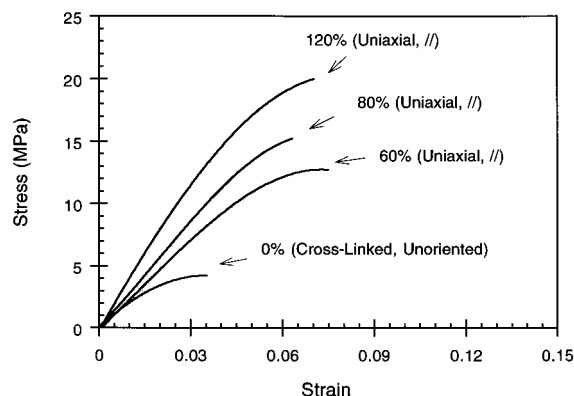


Figure 6. Stress-strain behavior of uniaxially oriented films prepared from TES (corn, 80% DS, air-dried).

with increase in the extension ratio during drying (from 0 to 120%), in a manner similar to those of the triethylamylose networks. In particular, a 3-fold increase in tensile strength, an 80% increase in modulus, and a 7.4-fold increase in toughness were observed at an extension ratio of 120%. The stress-strain curves also indicated a 2-fold increase in elongation at break, an improvement much smaller than that for the triethylamylose networks. A distinctive difference between the oriented TES (corn) and TEA films was the absence of any yield point in these oriented corn-derived specimens. Even at a higher stretching ratio (120%), material failure was observed at relatively low elongation at break, without the existence of a yield point. This might also be attributed to the higher amylopectin content in this material. For oriented corn starch-ether films, useful ranges of tensile strengths (12.80–20.00 MPa) and moduli (238–365 MPa) were nonetheless obtained. The elongations at break (3.5–7.5%) were low, documenting considerable brittleness, although the toughness of these TES (corn) films was considerably improved by the orientation process.

The oriented films prepared using wheat starch gave tensile strengths and moduli that, as usual, increased significantly with increase in extension ratio during drying from 0 to 120%. A 3-fold increase in tensile strength, a 90% increase in modulus, and a 7.4-fold increase in toughness were observed at an extension ratio of 120%. Elongation at break also increased, but only about 2-fold at that ratio. Tensile strengths of 7.87–11.70 MPa and moduli of 247–390 MPa were obtained. These values were significantly lower than those obtained for the oriented TEA films. Elongations at break (3.8–5.2%) were also low, underscoring the brittle nature of these oriented TES (wheat) films. In addition, no yield points were observed on the corresponding stress-strain curves.

Very similar results were obtained from rice starch. These oriented triethylstarch films exhibited a 3.5-fold increase in tensile strength, a 35% increase in modulus, and a 10-fold increase in toughness at an extension ratio during drying of 110%. The elongation at break, however, increased only about 2-fold at that ratio. The tensile strengths ranged from 8.69 to 16.74 MPa, and moduli from 304 to 319 MPa were obtained; these values were significantly lower than those obtained from the oriented TEA films. Elongations at break (3.6–8.0%) were also low, indicating these oriented TES (rice) films

Table 4. Percentage Amylose in Starches from Different Sources

starch sources	amylose content (%)	starch sources	amylose content (%)
amylose (pure)	100	rice starch	28 ^b
amylomaize VII	70 ^a	wheat starch	21 ^b
amylomaize V	50 ^a	amylopectin	0
corn starch	30 ^b		

^a Estimated by American Maize Co. ^b Estimated by Sigma Chemical Co.

were also relatively brittle. Similarly, there were no yield points on the TES (rice) stress-strain curves.

Results Obtained Using Amylopectin. Finally, orientation was applied to the triethylamylopectin networks. The diisocyanate cross-linking was successful in yielding networks from this polymer, but they were extremely fragile and brittle even in the swollen state. Orientation was therefore difficult to impose, and the swollen networks (at a polymer concentration of 0.2–0.25) usually broke before reaching a satisfactory stretching ratio. As a result, only films with relatively low extension ratios during drying could be studied. In contrast to all of the other materials, there was no good correlation between extension ratio during drying and improvements in mechanical properties. The failure to observe any significant improvements was attributed to the total absence of linear amylose.

Some Summarizing Comparisons. To differentiate the mechanical behaviors of the oriented TES and TEA films, two features should be recognized:

(1) The yield points that were exhibited in the highly oriented TEA stress-strain curves were absent in those for TES, regardless of the stretching ratio during drying. The oriented TES films exhibited considerably lower elongations at break, suggesting the relative brittleness of the films relative to the oriented TEA films at higher stretching ratios. Nevertheless, oriented TES films still showed considerable improvements compared to those before orientation.

(2) The oriented TES films exhibited lower ranges of tensile strengths and tensile moduli in comparison to the oriented TEA films. Among them, only TES (corn) exhibited relatively good mechanical properties. However, these oriented starch-ethers nonetheless acquired mechanical properties comparable to those of low-to-medium-density polyethylene.

The percentage of amylose in each starch source is listed in Table 4. The mechanical properties of the oriented TES are summarized in Table 5, along with the mechanical behaviors of TEA (pure) and TEA (amylomaize V), processed by either air-drying or coagulation. Clear trends can be noted from the information in Table 5; in particular, increases in amylose content very substantially increase the maximum values of the tensile strength and toughness exhibited by these materials.

It is illuminating to show the effects of amylose content on both the maximum values of the mechanical properties of the oriented TEA (TES) films, and the corresponding values obtained before orientation. Such information is shown in Figures 7–10, which show the effects of this compositional variable on tensile strength, tensile modulus, elongation at break, and toughness, respectively. These representations give, in particular,

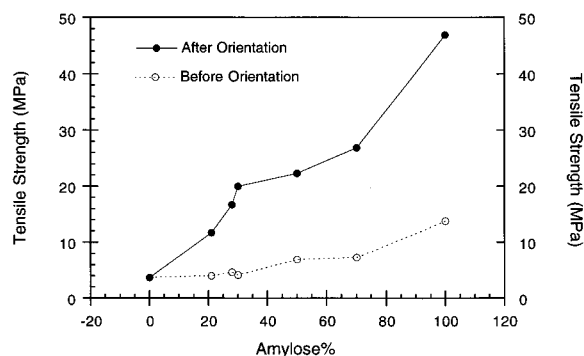


Figure 7. Values of the tensile strength obtained on oriented TEA (TES), as a function of amylose content.

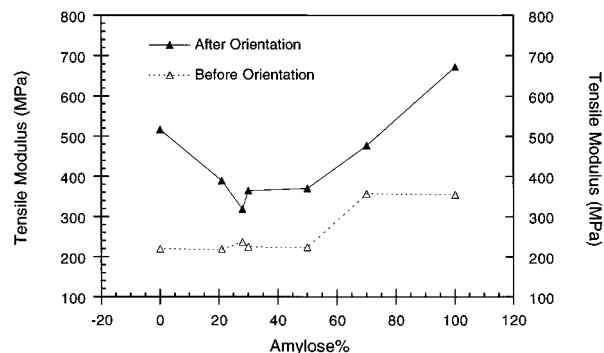


Figure 8. Values of the tensile modulus obtained on oriented TEA (TES), as a function of amylose content.

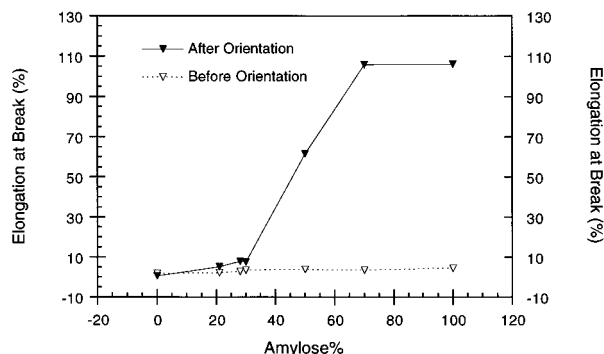


Figure 9. Values of the elongation at break obtained on oriented TEA (TES), as a function of amylose content.

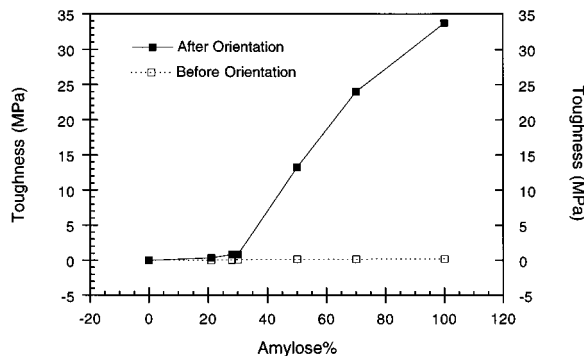


Figure 10. Values of the toughness obtained on oriented TEA (TES), as a function of amylose content.

a much clearer demonstration of the effects of amylose content on the performance of the oriented films.

As can be seen from Figure 7, increases in amylose percentage gave only small increases in the tensile strengths of the unoriented TEA (TES) films. After

Table 5. Mechanical Properties of Oriented Triethylstarch (Triethylamylose) Films with Various Amylose/Amylopectin Ratios

starch (amylose) source	extension ratio during drying (%)	yield strength (MPa)	elongation at yield (%)	strength (MPa)	elongation at break (%)	tensile modulus (MPa)	toughness (MPa)
amylomaize V, 80% DS	0			6.98	3.9	224	0.17
	70	13.49	11.1	13.31	12.4	276	1.24
	100	21.71	12.0	19.24	42.5	330	7.84
	135	25.65	14.2	22.30	61.6	371	13.27
amylomaize V, (coagulation process) ^a	55			11.14	7.7	233	0.60
	110	17.96	12.8	16.14	43.8	313	7.05
	135	29.56	12.4	18.95	40.5	400	7.43
amylose (pure), 70% DS	0			13.80	4.5	355	0.36
	45			21.95	8.9	432	1.20
	100	37.74	18.81	32.65	106.2	522	33.76
	140	49.00	22.25	46.95	76.6	673	32.42
starch (corn), 80% DS	0			4.20	3.5	225	0.10
	60			12.80	7.5	238	0.57
	80			15.21	6.3	270	0.53
	120			20.00	7.0	365	0.84
starch (wheat), 80% DS	0			4.01	2.2	219	0.05
	55			7.87	5.2	247	0.27
	100			9.70	3.82	332	0.21
	120			11.70	4.75	390	0.37
starch (rice), 80% DS	0			4.69	2.9	237	0.09
	60			8.69	3.6	304	0.17
	80			10.33	5.8	306	0.39
	110			16.74	8.0	319	0.85
amylopectin, 80% DS	0			3.71	1.9	220	0.037
	70			3.75	0.7	517	0.013

^a These values were obtained on oriented TEA (amylomaize V, 80% DS) films in which the solvent was removed from the swollen deformed samples by coagulation; the rest of the data in this table were obtained on oriented TEA or TES films finished by air drying.

orientation, the tensile strengths of the oriented materials also increased with increase in amylose content, but much more significantly. For the triethylamylopectin film (0% amylose), the tensile strength remained virtually unchanged, as expected, given the difficulties in orienting such highly branched chains. This is supported by the observation that increase in amylose percentage greatly enhanced the effects of orientation, as shown in the figure. A 3-fold to 4-fold increase in tensile strength was obtained for all the oriented TEA (TES) films (except TEAp), regardless of the amylose percentage. Only the absolute values differed. The higher the amylose content, the higher the tensile strength, and thus the stronger the film. As already mentioned, all the TEA (TES) exhibited lyotropic liquid-crystalline behavior above a certain degree of substitution, as did their corresponding networks. Thus, the failure to achieve significant improvements in mechanical properties for the triethylamylopectin films could possibly be attributed in part to the absence of liquid crystallinity.

The tensile moduli, on the other hand, did not show the same trends as the tensile strengths, especially for the oriented TEA (TES) samples. This is demonstrated in Figure 8. For unoriented samples, the moduli remained almost constant at low amylose percentage (<60%); only at higher percentages was there a noticeable increase. For the oriented samples, the moduli increased with increase in amylose content at higher percentages (>50%). The increases were 40–100%, which are not nearly as large as those for the tensile strength. At lower amylose contents (<30%), the moduli may again have increased, but in this case unexpectedly. At 0% amylose (i.e., triethylamylopectin) a 135% increase in modulus was actually obtained, at a stretching ratio during drying of 70%.

As shown in Figure 9, all the unoriented TEA (TES) films broke at very small strains (1.9–4.5%), demon-

strating their brittleness. Orientation, however, was also effective at giving dramatic increases in the elongation at break at higher amylose contents. Finally, as already mentioned, toughness is arguably the most important mechanical property from the engineering point of view. None of the unoriented TEA (TES) films had any significant toughness, as is documented in Figure 10, regardless of their amylose content. A profound improvement in toughness, is seen to be obtained by orientation of higher-amylose films. 80-fold to 100-fold increases were, in fact, obtained at the highest amylose contents!

Concluding Remarks and Outlooks

In this third part of the three-part study, the influence of degree of substitution and amylose/amylopectin ratio on the mechanical properties was carefully examined. The degree of substitution had virtually no effect on the mechanical properties of the oriented triethylamylose (amylomaize VII) films. On the other hand, the amylose/amylopectin ratio exerted a strong effect on their performance characteristics. Generally, the higher the amylose content in the starting material, the larger the increases and absolute values of the mechanical properties obtained after orientation. In view of the cost, availability of the starting material, and final performance, it appears that three kinds of starch (amylose) ethers have promising commercial potentials: amylomaize VII, amylomaize V, and corn starch. The increased hydrophobicity of these oriented starch-ethers relative to starch itself should permit them to maintain satisfactory performance during processing, storage, and use. They could thus represent biodegradable materials suitable for replacing conventional synthetic polymers.

Table 6 summarizes the approximate costs, production levels, and mechanical properties of some commercially available biodegradable materials. As can be

Table 6. Approximate Costs, Production Levels, and Mechanical Properties of Some Commercially Available Biodegradable Materials Possibly Useful as Packaging Films^a

	cost (\$ per lb)	production level (lb per year)	T_g (°C)	tensile strength (MPa)	elongation at break (%)
starch	0.15	>230 billion	230	NT ^b	NT
cellulose acetate (DS = 2.5)	1.70	2.3–2.4 billion	190	17–25	10–30
poly(vinyl alcohol)	1.50–2.50	150–200 million	58–85	40–50	300–400
polycaprolactone	2.70	<10 million	–60	21–31	600–1000
poly(lactic acid)	1.00–3.00	10 million	50–59	50	3
triethylamylose ^c			~40	22–47	7.7–120
triethylstarch ^c			~40	11–20	3.5–8.0

^a Most data were obtained from ref 3. ^b NT means not testable (extruded films unavailable). ^c Mechanical property values were obtained from oriented films using the novel orientation technique.

Table 7. Approximate Costs, Production Levels, and Mechanical Properties of Some Conventional Synthetic Polymers

	cost (\$ per lb)	production level (lb per year)	yield strength (MPa)	elongation at yield (%)	strength (MPa)	elongation at break (%)	tensile modulus (MPa)
LDPE ^a			6.2–11.5	100–800	6.9–16	100–800	102–240
MDPE ^a	0.50–0.60	40–45 billion	10–19	50–600	8.7–21	50–600	205–370
HDPE ^a			28–40	5–8	25–45	50–900	900–1200
polystyrene ^b	0.40–0.50	10–12 billion			35–57	1.6–2.4	2400–3340
triethylamylose ^c			25.6–49	14–23	22–47	7.7–120	370–673
triethylstarch ^c					11–20	3.5–8	319–390

^a These data were obtained from ref 13. LDPE: low-density polyethylene; MDPE: medium-density polyethylene; HDPE: high-density polyethylene. ^b These data were obtained from ref 14. ^c These data were obtained on oriented TEA and TES.

seen, the oriented starch–ether films have mechanical properties comparable to cellulose acetate, poly(vinyl alcohol), etc. In addition, and in contrast to most existing biodegradable materials (mainly polyesters), the preparation of these novel starch materials does not require consumption of natural resources such as oil, which will obviously be economically advantageous. Also relevant in this regard are polyethylene and polystyrene, two of the most commonly used commercial polymers. Their mechanical properties are summarized in Table 7. Comparisons among these results demonstrate that oriented starch–ethers having higher amylose/amylopectin ratios (>1) have mechanical properties that are very similar to those of high-density polyethylene. Both polymers exhibit yield points, and they have very similar values of yield strengths, elongations at yield, strengths at break, and comparable values of the tensile modulus. For oriented starch ethers with lower amylose/amylopectin ratios (<1), strengths at

break, and tensile moduli are comparable to those of low-to-medium-density polyethylene.

There are a number of applications where these oriented starch-ethers could be used, including disposable food-service items, beverage-can harnesses, grocery bags, diaper backings, packaging films, and agriculture mulch films. Most of these items are currently produced from nonbiodegradable polyethylene or polystyrene.

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