THERMOPLASTIC XYLAN DERIVATIVES AND RELATED BLENDS

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(ABSTRACT)

The relationship between substituent chemistry and melt behavior for xylan derivatives was investigated by differential scanning calorimetry and parallel-plate dynamic viscometric measurements. Xylan esters exhibit characteristic T_g values which decrease with increasing size of substituent. However, these materials do not flow at temperatures well above T_g. The ether derivative hydroxypropyl xylan was found to flow at substitution levels higher than 0.5 degree of substitution, with melt viscosity decreasing as the degree of substitution increased.

The influence of viscosity ratio and composition on the texture of melt-blends of hydroxypropyl cellulose and polystyrene was studied for viscosity ratios of 0.08 to 0.55. Blends were examined by SEM and TEM. It was found that composition was the determining factor in texture, and not viscosity ratio over the range tested. Extrusion
problems limited the range of compositions tested to 40% biopolymer or less. Phase inversion was not observed, although inversion was expected for some samples based on predictive models in the literature.
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1.0 INTRODUCTION

1.1 Biopolymers in melt blends

The most abundant polymers in the world are cellulose and lignin, the two structural biopolymers of the plant kingdom. The plant kingdom also provides numerous other polymers as hemicelluloses. These polymers are created by energy-efficient processes, as renewable resources, and in their native state are biodegradable. For environmental reasons it is essential that society learn to use these polymers.

A convenient route to introduce biopolymers into conventional plastics is melt blending. Most biopolymers are not thermoplastic, but chemical modification yields some derivatives which are thermoplastic and can be melt-processed.

Xylan is the prevalent hemicellulose in hardwoods. (1). Recently, xylan has been chemically modified to give thermoplastic derivatives (2). In many cases once a biopolymer is chemically modified, it is no longer biodegradable (3). However, some xylan derivatives have been shown to be biodegradable, unlike corresponding derivatives of other biopolymers. Only xylan has been
shown to give both thermoplastic and biodegradable derivatives. Thus while this work includes several thermoplastic polysaccharides, xylan derivatives are given particular attention.

1.2 Incompatible melt blends

In recent years there has been considerable research in the area of polymer blends. The development of novel polymers is expensive and time-consuming, and currently most truly new polymers are intended for specialty applications. For many applications, the development of an appropriate polymer is accomplished by combining two or more existing polymers. This can occur by various copolymerization schemes, or more simply by physically blending the pure components.

Most polymer systems are incompatible; when mixed, the components will not form a single homogeneous phase, but rather will form a two-phase material (4). Provided both polymers are thermoplastic, the polymers can be mixed by mechanical action in the melt state.

The structure, or texture of a polymer blend depends on many factors: composition, processing history,
interfacial tension between components, and the viscosity and elasticity of the melts. The viscosity ratio and composition of the blend are key variables in the texture, and determine which component will be the continuous phase (5). This phase continuity has been reported as an important factor in the biodegradation of blends (6,7).

1.3 Objectives and Justification

The objective of this study is to examine some factors involved in melt-processability of polysaccharides, especially xylan derivatives. The results of this study are critical in designing biopolymers, particularly modified polysaccharides, for applications in polymer blends.

Specifically, the following questions are investigated:

1. The effect of level of substitution and type of substituent on the melt viscosity of xylan derivatives.

2. The effect of viscosity ratio and composition on the texture of a melt-blend of a polysaccharide derivative and polystyrene.
The knowledge gained in these two related but different studies will lead to the design of xylan derivatives for applications in polymer blends, utilizing the rare combination of thermoplasticity and biodegradability.
2.0 BACKGROUND

For years, polymer scientists have been developing polymers and plastics for countless applications. Properties such as durability, chemical resistance, and ultraviolet stability have been key targets in this development. However, the very properties which can make a plastic desirable in use can be a problem when it comes to disposal. Recently, the scientific community has focused increasing attention on the problems of plastics waste management, including the options of recycling and environmentally degradable plastic formulations. In addition, some biodegradable plastics are being developed for medical applications including internal sutures, temporary implant devices, and controlled-release pharmaceuticals.

2.1 The Need for Degradable Plastics

A recent study (8) reported that, of municipal solid waste discarded in 1984, 7.2 percent by weight was plastic material from packaging and durable goods. Additionally, an unknown amount of plastics are discarded as litter.
This litter creates aesthetic problems, and in certain cases can pose a hazard to wildlife. At least 11 states have enacted legislation requiring plastic loop can carriers to be degradable due to the problems of animals becoming entangled, and several European countries have restrictions or bans on nondegradable plastics in certain disposable packaging. Further legislative limitations on disposable plastics are expected in the near future. It should be noted that degradation is only one of several required approaches to plastic waste reduction; recycling will probably have a far greater impact than degradation, as technology for reprocessing mixed scrap plastic is developed.

2.2 Options for degradable plastics

There are currently two technical options for producing degradable plastics. Either the plastic itself must degrade in some fashion, or the plastic may be combined with a component that degrades, causing the end product to deteriorate. This degradation can be caused by biochemical means, or by other nonbiological means.

2.2.1 Photodegradation

Currently polyethylene is available in specialty grades which degrade upon exposure to ultraviolet light.
Polyethylene can be made photodegradable by two means; by the addition of uv-unstable links in the backbone, or by the use of prooxidant additives. An all-carbon backbone is stable to ultraviolet light. However, if carbon monoxide is used as a comonomer, C=O functionality is introduced. This functionality causes chain scission when exposed to uv light for extended periods, and thus a degradation of the polyethylene chains to smaller units which are more easily degraded by microorganisms. Typically the C=O units are incorporated at levels less than two percent (8). The polyethylene will degrade at rates depending on the amount and intensity of sunlight to which it is exposed, the temperature, and the level of carbon monoxide used.

Another means of causing chain scission of polyethylene is to incorporate an additive that will decompose in uv light and subsequently catalyze chain scission. Two recent patents (9) describe the use of a two-component system, one an iron complex which acts as a photoinitiator, and one a metal ion deactivating compound which acts as a stabilizer. By varying the ratio of the two additives, it is claimed that degradation rates can be tailored to meet local conditions and requirements.
In any case, photodegradation of polymers can occur only in the presence of light, a condition that is not met when the plastic is buried in a landfill.

2.2.2 Biodegradation

Biodegradation in its strictest definition refers to the degradation of a material caused by the action of living organisms (10). Typically, the organisms are bacteria or fungi. Most biodegradable polymers contain hydrolyzable links in their backbone; polyureas, polyurethanes, and polycaprolactones are common polymer types which have the potential to be biodegradable. In addition, the natural polymers such as starch and cellulose are biodegradable in their unmodified form.

A number of factors affect the biodegradability of a particular polymer sample. Some of these factors are purely chemical, while some are morphological.

2.2.2.1 Chemical factors

For a polymer to be biodegradable, it must be susceptible to the action of enzymes. This requires that hydrolyzable or oxidizable bonds must be present in the backbone, and the polymer chains must have sufficient conformational flexibility to fit the enzyme sites.
Hydrophilic polymers are much more likely to biodegrade than hydrophobic ones, due to the increased accessibility and mobility of the enzymes in a system with significant water present.

Molecular architecture also plays a role in degradation. In general, biodegradation decreases as molecular weight increases, and degradation is inhibited by chain branching (11).

2.2.2.2 Morphological factors

A critical factor in degradation is accessibility to enzymes. The surface area available for attack, and the crystallinity of the sample have dramatic effects. Degradation of semicrystalline polymers occurs in the amorphous regions; SEM photographs of partially degraded spherulites of poly(ε-caprolactone) show this clearly (11). (Figure 1.)

In phase-separated blends of a biodegradable component dispersed in a much more slowly degrading component such as polyethylene, the biodegradable polymer will be selectively removed first. This can lead to physical disintegration of the material. Additionally,
Heavy mycelial growth on a PCL700-coated agar plate. (a) Diffuse biodegradation at the amorphous areas exposing spherulite arms is seen; 285X. (b) Early signs of crystalline areas being biodegraded. Amorphous areas severely degraded; 1080X.

Figure 1. Degradation of poly(ε-caprolactone). Copied without permission from reference 12.
this creates more exposed surface area, which accelerates the breakdown of the more stable component. Narayan (6) is currently working on encapsulating a chain scission catalyst for polyethylene in the dispersed starch domains of a starch-polyethylene blend. The catalyst is freed to work on the polyethylene only after the starch is biodegraded, extending the useful life of the material while accelerating its eventual breakdown.

Studt (6) also discusses the work of Wool and Long, who are working on high-starch content blends of polyethylene. Using percolation theory (a mathematical technique used to study the "connectedness" of randomly distributed objects) (13), Long has predicted the composition range over which starch becomes a continuous phase, thus dramatically accelerating the breakdown of the material. This occurs around 59% by volume.

Tokiwa (7) has studied the effect of phase structure on the biodegradation of blends of polycaprolactone and low-density polyethylene, and biodegradation of cornstarch-containing polyolefins. He showed that the PCL-LDPE films were only biodegradable when the PCL was a continuous phase, and this could be manipulated by the viscosity ratio of the PCL and LDPE. He also showed that
only the cornstarch granules on the surface of films were degraded, and that the biodegradability of these films increased remarkably when the starch loading reached 40 wt percent. Presumably this was due to the contact between neighboring granules at this concentration. The starch blends were made by roll-milling rather than extrusion.

2.3 Polysaccharides in biodegradable plastics

The recycle of dead plant material is essential to the balance of nature; thus natural polymers are by design biodegradable. Cellulose and starch have been investigated for several decades as possible components of biodegradable plastics, and blends of small amounts of starch with polyethylene are finding some commercial application as agricultural mulch film.

2.3.1 Starch

Narayan (15) has recently reviewed the progress of starch-based plastics. Starch is an abundant and cheap raw material made up of amylose and amylopectin. Both of these are \( \alpha -1,4\)-D-glucose polymers; amylose is linear and comprises about 25 percent of starch whereas amylopectin is branched. Starch was first developed as a filler for polyethylene films by Griffin (16). He was able to incorporate up to 10 percent starch into
polyethylene for agricultural mulch film, and his technology is used in the biodegradable plastic film products marketed by St. Lawrence Starch Co. Otey, et al. (17,18,19) and Westhoff et al. (20) extended Griffin’s work by incorporating levels of starch up to 90 percent, and by getting the starch to disperse in the polyethylene by a variety of means, rather than simply act as a particulate filler. Their best films were made by mixing starch and poly(ethylene-co-acrylic acid) in water, then adding aqueous ammonia to neutralize some of the acrylic acid. Low-density polyethylene pellets were added and the mixture was extruded 2-3 times until a uniform melt was obtained. This blend was then extruded and blown into film. Films made with 40 percent starch and up to 40% polyethylene were clear, flexible, and uniform (19). According to Narayan (15), Agritech Industries is attempting to commercialize this technology. There is considerable incentive to develop a biodegradable film for agricultural mulch which could simply be plowed under after use; removal costs for polyethylene mulch film are over $100 per acre.

Another approach to incorporating starch into plastics is to chemically react it in some way. Narayan
(15) has summarized a large quantity of work in this area, ranging from the use of starch as crosslinks in a polyurethane to the use of a modified starch-g-polyacrylonitrile as an aqueous fluid absorbent. Of more direct interest is Narayan’s own work and the work of Stannett, Gilbert, and their colleagues. Most of the work described below for cellulose was paralleled with amylose.

Lynn (21) and Lee (22) synthesised biodegradable block copolymers from amylose and polyesters, poly(propylene glycol), and polybutadiene. Narayan (23) has further described the synthesis of tailor-made graft copolymers of starch and anionically prepared segments of other species. Applications as compatibilizers for polysaccharides with commodity thermoplastics are being sought.

2.3.2 Cellulose

Potts, et al. (24), in a survey commissioned by the U.S. Environmental Protection Agency, first suggested the approach of using biopolymer blocks to synthesize biodegradable plastics. Kim (3) proceeded to synthesize biodegradable block copolymers from cellulose. Kim depolymerized a fully acetylated cellulose to produce segments with terminal -OH groups only. These groups were
then capped with a diisocyanate and reacted with a monofunctional segment such as an isocyanate-capped polyester. The resulting ABA block copolymer was treated with sodium methoxide to deacetylate the cellulose block, resulting in a biodegradable cellulose segment. The copolymers were incubated with cellulysin and the degradation was monitored by intrinsic viscosity measurements, and the polymers were found to be more biodegradable than normal cellulose. These polymers were patented (25). Further research by the same group found that the higher degradation could be attributed to the lower crystallinity of the short cellulose blocks, resulting in increased moisture sorption and greater accessibility than normal cellulose (26).

This research program was extended to include the starch block copolymers discussed earlier and cellulose graft copolymers. Penn (27) synthesized cellulose graft copolymers using a partially-acetylated cellulose (degree of substitution 2.27). The free -OH groups were capped with a diisocyanate and subsequently reacted with a monofunctional, -OH-capped segment of poly(ethylene glycol) or poly(butadiene-styrene). The cellulose backbone was then deacetylated, and the resulting
copolymer was shown to be biodegradable. A second paper (28) discussed a similar scheme, only the grafted segments were added by free-radical polymerization of styrene rather than condensation of a pre-polymerized segment.

Narayan et al. (23) have extended this general scheme for grafting onto cellulose by controlling both the site of grafting and the structure and size of the grafted segment. In a multistep process, the cellulose was fully acetylated, then deacetylated under very mild conditions to regenerate only the most active hydroxyl group, on C6 of the anhydroglucose unit. The product was then reacted with methylsulfonyl chloride to provide a mesylated cellulose acetate. Segments of polystyrene and poly(methyl methacrylate) were anionically prepared in order to control the segment length within a narrow distribution, and then terminated with an active group. The segments were grafted to the cellulose by a nucleophilic displacement of the mesylate group on C6 (29). This chemical scheme is also described for starch, and part of the incentive for producing these tailor-made copolymers is to create compatibilizers for blends of thermoplastics with starch or cellulose derivatives.
2.5.3 Xylan

Xylan is the prevalent hemicellulose in hardwoods, and serves as a natural coupling agent between cellulose and lignin in wood cell walls. Chemically, xylan is poly(β-1,4-D-xylose) with an occasional 4-O-Methyl glucuronic acid side chain. Structurally xylan is similar to cellulose but has only two hydroxyl groups per repeat unit, as shown in Figure 2. Naturally occurring xylan has about seven acetyl groups for every ten xylose units, although these groups are often stripped in the separation and isolation process. Isolated xylan is crystalline and the crystalline structure was first described by Marchessault (30). In its native state, xylan has a degree of polymerization (DP) somewhat above 200 (31). Historically, xylan has been isolated by extracting wood meal with mild alkali, then precipitation into an alcohol. Xylan oligomers can be isolated from the aqueous extracts of steam-exploled hardwoods (2), and a number of applications are being explored.

Chemical modification of xylan was first reported by Huseman (32) as a means of making the material soluble so that molecular weight could be determined. Methyl ethers of wheat straw and beechwood hemicellulose were used in viscometric and osmotic determination methods. Esters
Figure 2. Hardwood xylan, showing 4-O-methylglucuronic acid side branch and natural partial acetylation.
were made (33) but proved to be only partially soluble. Carson and Maclay (34) made a wide variety of hemicellulose esters from corncob and bean hemicelluloses, for sugar analysis and molecular weight determination. They also report insolubility in a variety of solvent systems. None of these investigators report any investigation of properties for the derivatized hemicelluloses or xylan other than solubility.

Of the three major components of hardwood, xylan degrades first in pulping (1), rotting (35) and pyrolysis (36), ahead of lignin and cellulose. Additionally, preliminary data (37) indicates that some xylan derivatives are biodegradable, unlike corresponding modified cellulosics. This suggests possibilities as a biodegradable component in plastics, an application which has been studied for cellulose and starch.

2.4 Controlling the texture of a blend

The texture of a melt blend is affected by a number of parameters, including rheological and interfacial properties of the components, processing conditions, and composition. The following is by no means a comprehensive
review, but rather a brief review of some key work which has proven relevant to the current study.

2.4.1 Droplet breakup and viscosity ratio

The early work on deformation and break-up of liquid droplets in another liquid was done by Taylor (38,39). He studied the deformation of initially spherical Newtonian droplets in Newtonian matrix fluids undergoing shear flow. The droplets deformed into spheroids, and Taylor expressed the deformation $D$ as

$$D = \frac{L-B}{L+B}$$  \hspace{1cm} (1)

where $L$ is the major and $B$ the minor axis of the spheroid. For small deformations, this can be related to interfacial tension and viscosity by

$$D = \frac{2Cu(19u'+16u)}{T (16u'+16u)}$$  \hspace{1cm} (2)

where $u$ is the matrix and $u'$ the dispersed drop viscosity, $C$ is the shear rate, $T$ is the interfacial tension, and $a$ is the initial drop viscosity. Introduction of the viscosity ratio $VR$ ($VR=u'/u$) gives (40)

$$D = \frac{uCa}{T} \frac{(19VR+16)}{16(1+VR)}$$  \hspace{1cm} (3)
Taylor also discussed the break-up of droplets, suggesting that this occurs when the viscous shearing forces become greater than the interfacial tension holding a deformed droplet together. For very low viscosity ratios (VR=0.0003), the droplets deformed into long, thread-like strings but did not burst. Taylor also predicts that, at very high viscosity ratios the droplets will not burst, and the equilibrium deformation will be dependent only on viscosity ratio:

$$D = \frac{5u}{4u'}$$  \hspace{1cm} (4)

Karam and Bellinger (41) studied a number of systems and experimentally determined that the viscosity ratios which allow droplet breakup are $0.005 < VR < 4$, regardless of the system for Newtonian fluids. Their data show that the most favorable range for breakup is $0.2 < VR < 1$. Taylor's ideas were further studied for break-up in shear flow of viscoelastic fluids by Flumerfelt (42), who found that there is a minimum drop size below which no further burst will occur. He also found that droplets generally break up at lower stresses in viscoelastic fluids than in Newtonian systems.
2.4.2 Morphology of incompatible melt blends

Vanoene (43) extended the study of droplet breakup and dispersion to polymer melt mixtures, studying the effect of the normal stress functions on breakup and dispersion for polymer melt mixtures. White and Min (4) have recently reviewed the processing of incompatible melt blends. They discuss the use of the capillary, or Taylor, number as a dimensionless ratio of interfacial to viscous forces in fluid systems. Wu (44) uses the reciprocal, which he calls the Weber number, in a study of both interfacial and rheological effects on dispersion:

$$N_{\text{We}} = \frac{1}{N_{Tal}} = \frac{n_m a \dot{\gamma}}{\sigma}$$  \hspace{1cm} (5)

where \(n_m\) is the matrix viscosity, \(a\) is the average radius of the dispersed phase, \(\dot{\gamma}\) is the shear rate, and \(\sigma\) is the interfacial tension between the phases. Wu uses data on several rubber-containing blends to show the effect of interfacial and rheological properties on the dispersed-particle size. Plotting the Weber number versus the viscosity ratio, Wu obtains the master curve shown in Figure 3. This relationship is described by the equation

$$\left( \frac{n_m a \dot{\gamma}}{\sigma} \right) = 4 \left( \frac{\eta_d}{\eta_m} \right)^{\pm 0.84}$$  \hspace{1cm} (6)
Figure 3. Dimensionless master curve of $N_{We}$ versus viscosity ratio for melt extrusion using a co-rotating twin-screw extruder. Copied without permission from reference 44.
Han (45) has done extensive work on the processing of multiphase polymer melts. Of interest is his 1977 paper (46) on the morphology and properties of two-phase injection-molded blends, in which he describes the effects of mixing device on the observed texture. He also determines that scatter in data from the blends can be attributed to the degree of dispersion in the blend.

Phase continuity is an important issue in the properties of blends. Sperling (5) suggests a relationship between the ratio of zero-shear viscosities of a binary melt blend and the composition of phase inversion

\[
\frac{\eta_A}{\eta_B} = \frac{\phi_A}{\phi_B} \tag{7}
\]

where \( \eta_A \) and \( \eta_B \) are the zero-shear viscosities and \( \phi_A \) and \( \phi_B \) are the volume fractions of the two components. This agrees with experimental observations that the less-viscous phase tends to form the continuous phase, even under conditions where it is not the major component by volume. Miles and Zurek (47) have experimented with compositions near the point of inversion, and suggest that Sperling's relationship be modified to reflect the actual viscosities present under mixing conditions:
\[ \frac{\eta_4(\dot{\gamma})}{\eta_5(\dot{\gamma})} = \frac{\phi_4}{\phi_5} \]  \hspace{1cm} (8)

They have data on a number of blends which show that dual-phase continuity can readily be achieved at the composition of phase inversion. This dual-phase texture has potential application in conductive polymers and controlled-transport membranes. It could also be of interest to those researchers interested in biodegradation. While it is an unstable texture in the melt, it can be frozen in, as the time scale for coalescence in the melt is on the order of thirty minutes or more, depending on the system.

2.4.3 Melt rheology of incompatible blends

Han and Kim (48) studied the viscosity and elasticity of a number of blends and noted that there is not always a monotonic relationship between viscosity and composition; in fact, there are often maxima and minima present in a graph of viscosity versus composition at a particular shear rate. Using die swell as a measure of melt elasticity (the recoverable mechanical energy storage in the melt), the elasticity versus composition behavior was found to complement the viscosity behavior. The minimum viscosity occurs at the same composition as the maximum
elasticity, and vice versa. They conclude that the viscoelastic properties of the blend depend on the particular type of morphology present. Plochocki (49) shows direct SEM data which confirms that the compositions where maximum synergism or antagonism (deviation from linear additivity) is observed in the viscoelastic properties coincide with changes in the texture of the blend. Utracki (50) reviews previous reports of viscosity-composition relationships for blends, and divides the systems into three types. Positive-deviation blends (PDB) show viscosity that is monotonically greater than that expected from additivity. This behavior is seen in systems where the polymers are miscible, and sometimes in systems that are heterogeneous but at a very small scale, such as compatibilized blends. Negative-deviation blends (NDB) are those systems where the viscosity is less than that expected from additivity, and this behavior is typical of most incompatible melt blends. In a few cases, both positive and negative deviation is seen in the viscosity, depending on the composition. This type of behavior is related to phase inversion. Thus an examination of the viscosity-composition behavior of some polymer systems may give information on the melt texture of the blend.
3.0 MATERIALS AND METHODS

This chapter documents the materials and methods used in this research project.

3.1 Xylans

All of the xylan derivatives were made from an unbleached xylose-rich pentosan isolated from barley husks by alcohol precipitation and supplied by Alko, Ltd of Helsinki, Finland. The derivatives were prepared and the degree of substitution determined by Dr. Rajesh K. Jain of the Wood Chemistry research group.

3.1.1 Esters

Xylan esters were prepared by acylation of xylan according to the following procedure, described for acetate derivative: 1.0 gram xylan was dried overnight at 50°C on a vacuum oven, then placed in a dry three-neck flask fitted with a condenser, thermometer, and dry nitrogen purge. Purge outlet was through a bubbler off the condenser. Dry formamide (10.0ml) was added and stirred at 40°C for 6 hours to dissolve the xylan. Dry pyridine (5.0ml) was added, and the reactor was cooled to
0°C in an ice bath. Acetic anhydride (10.0 ml) was added, and the mixture was stirred at this temperature for about six hours. The reaction was continued overnight at ambient temperature. After 24 hours, an additional 10.0 ml acetic anhydride was added. The reaction was continued at ambient temperature for an additional 12 hours, after which the reactor was heated to 50°C for a final 12 hours. The reactor contents were precipitated into 250 ml 1% aqueous HCl at 0°C. The resulting product was collected by filtration, washed with water, and dried overnight at 50°C in a vacuum oven.

To make the other alkyl esters, the appropriate acid anhydride (propionic, butyric, hexanoic) was used in place of the acetic anhydride in the same procedure.

3.1.2 Ethers

Hydroxypropyl xylan (HPX) was prepared by Dr. Jain according to the following procedure: 75 grams of xylan were dried overnight at 50°C in a vacuum oven, then placed in a dry three-neck flask fitted with a condenser, thermometer, and dry nitrogen purge. Purge outlet was through a bubbler off the condenser. Aqueous 1N KOH solution (300 ml) was charged to the flask and stirred at
40°C for 12 hours until the xylan was completely dissolved. The reaction mixture was cooled to 0°C in an ice bath and 100 ml propylene oxide (PO) was added dropwise over a period of 2 hours. About 1 hour after completing PO addition, the flask was allowed to return to ambient temperature and stirred for 16 hours. The reactor was cooled to 0°C, and an additional 50 ml PO was added dropwise. The reactor was allowed to regain room temperature, and stirred for an additional 32 hours.

The reaction mixture was precipitated into 4000 ml acetone with brisk stirring provided. A slurry was formed which was washed by four successive washings and decantations with 300 ml portions of fresh acetone. The precipitate was collected by filtration and dried at 40°C in a vacuum oven for 24 hours.

Different degrees of substitution of HPX were achieved by varying the pH of the reaction mixture from 10.0 to 12.5. Higher substitution occurred at higher pH. This was varied by using concentrations of KOH in the initial charge to the reactor which varied from 0.5N to 1N.
The hydroxypropyl xylan was in some cases further modified by esterification. In these cases, the esterification was done according to the procedure described for esterification of unmodified xylan except that formamide was not used, and the volume of pyridine was increased to achieve equal concentration of polysaccharide.

3.2 Commercial Polymers

Several commercial polymers were used in the course of this project, as described below.

3.2.1 Hydroxypropyl cellulose

The hydroxypropyl celluloses were supplied by Aqualon, and are sold under the trade name KLUCEL. The properties of the three grades are described in Table I.

3.2.2 Polystyrenes

The polystyrenes were supplied by The Dow Chemical Company, from a selection of general-purpose resins sold under the tradename STYRON. The properties of the five grades used are described in Table II.
Table I. Hydroxypropyl celluloscs used.

<table>
<thead>
<tr>
<th>Designation</th>
<th>$M_w^1$</th>
<th>$M_n^2$</th>
<th>$M_w^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HPC-G</td>
<td>370,000</td>
<td>233,400</td>
<td>846,600</td>
</tr>
<tr>
<td>HPC-H</td>
<td>1,150,000</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>HPC-L</td>
<td>95,000</td>
<td>88,600</td>
<td>207,500</td>
</tr>
</tbody>
</table>

$^1$as reported in Aqualon literature.

$^2$Determined by GPC as described in 3.3.1

NA - this data is not available due to lack of solubility in THF.
Table II. Polystyrenes Used

<table>
<thead>
<tr>
<th>Designation</th>
<th>Dow grade</th>
<th>Melt Index</th>
<th>$M_n$</th>
<th>$M_w$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS1</td>
<td>615-APR</td>
<td>15</td>
<td>72,400</td>
<td>188,000</td>
</tr>
<tr>
<td>PS2</td>
<td>xp6065.01</td>
<td>8</td>
<td>105,000</td>
<td>204,000</td>
</tr>
<tr>
<td>PS3</td>
<td>623</td>
<td>4.5</td>
<td>151,000</td>
<td>331,000</td>
</tr>
<tr>
<td>PS4</td>
<td>685</td>
<td>2.4</td>
<td>105,000</td>
<td>228,000</td>
</tr>
<tr>
<td>PS5</td>
<td>613</td>
<td>1.5</td>
<td>225,000</td>
<td>426,000</td>
</tr>
</tbody>
</table>

1 as reported in Dow literature.

2 determined by GPC as described in 3.3.1
3.3 Characterization of Polymers

All of the polymers used were characterized according to the following methods, where appropriate.

3.3.1 Molecular Weight

Molecular weight was measured by size-exclusion chromatography on a high-pressure liquid chromatography system utilizing a series of three columns (10^3Å, 10^4Å, 10^6Å), a Waters model 410 differential refractometer, and a Viscotek model 100 differential viscometer. The system was calibrated with polystyrene standards using universal calibration and run with tetrahydrofuran as the mobile phase. A flow rate of 1.0 ml/minute was used.

3.3.2 Degree of Substitution

For the polysaccharides, degree of substitution was determined by proton nuclear magnetic resonance spectroscopy and fourier-transform infrared spectroscopy. This analysis was performed by Dr. Rajesh K. Jain. FTIR spectra were obtained using a Nicolet 5SXC spectrophotometer. Approximately 1mg dry sample was dispersed in 200 mg KBr and pressed into a pellet. This pellet was examined by FTIR to indicate essentially complete substitution of all -OH groups of an acetylated sample. This was determined by the absence of a broad
band at around 3200 sec$^{-1}$. NMR spectra were obtained using a Bruker WP270 spectrometer operating at 270 Mhz on 10 % w/v solutions of sample in deuterated chloroform. Typically, about 100 free-induction decays were recorded. The degree of substitution was determined by comparing the integrated area of the peak indicating $-\text{CH}_3$ groups on acetyl substituents to the integrated area of the peak indicating $-\text{CH}_3$ groups on propoxy groups.

3.3.3 Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) was used to determine the thermal transitions in the polymers. A Perkin-Elmer DSC-4 interfaced to a TADS data station was used to collect the data. 10-15 mg samples were pre-scanned from $-50^\circ$ to $200^\circ\text{C}$ at $10^\circ\text{C}$ per minute, then quenched to $-50^\circ\text{C}$. The second heating scan at the same rate was used to determine the glass transition temperature. The samples were run under dry nitrogen. The glass transition temperature was defined as the temperature at which one half the total change in slope had occurred.

3.3.4 Melt Flow

Approximately 50 mg of sample were placed in the
center of a fluoropolymer sheet and covered with several grams of low-density polyethylene pellets. The sample was sandwiched with a second fluoropolymer sheet and aluminum plates, placed in a Carver Model C laboratory press at 180°C for 1 minute to preheat, then pressed to 5000 pounds pressure for 1 minute. After removal from the press and cooling, the resulting film was inspected to see whether the derivative flowed or simply spread as particles imbedded in the polyethylene. This is simply a yes/no test to see if the derivative will flow under the applied conditions of heat and pressure.

3.3.5 Melt Viscosity

The viscoelastic properties of polymer melts were measured using a Rheometrics RMS-800 rheometer. Frequency sweeps from 0.1 to 500 hertz were run at a strain of one percent. The geometry was parallel plate, with a radius of 12.7 mm and a gap of 1.6 mm. The sweeps were run at constant temperature, at temperatures ranging from 150°C to 190°C, depending on the experiment. Additionally, strain sweeps from zero to ten percent strain at 10 hz and 190°C were run for several samples.

The measured viscoelastic properties were used to determine the shear rate dependent viscosity by
application of the Cox-Merz rule, which states

$$
\eta (\dot{\gamma}) = \eta^*(\omega) \bigg|_{\omega = \dot{\gamma}}
$$

(9)

where $\eta$ is the viscosity, $\dot{\gamma}$ is the shear rate, $\eta^*$ is the dynamic viscosity, and $\omega$ is the frequency (51).

3.4 Blending and Fabrication

3.4.1 Melt Blending

Melt blends were made by extruding the polymers. Initially, the polymers were dry blended, then extruded through a Custom Scientific Instruments model CS-194 melt extruder operating at 70 RPM and 180°C. The extrudate strand was pelletized, the pellets were tumble-mixed, and re-extruded. The final extrudate was pelletized.

3.4.2 Compression Molding

The pelletized blends were compression-molded into discs 25 mm in diameter and 1.6 mm thick. A Carver model C laboratory press, at 180°C was used. Pellets were placed in a template that was sandwiched between
fluoropolymer release films and aluminum backing plates. The sandwich was placed in the press and allowed to preheat for 90 seconds. The pressure was then increased to 5000 pounds and held for one minute. The pressure was released, and the sandwich was removed from the press. The backing plates were removed and the sample was cooled until firm and popped out of the template.

3.4.3 Injection Molding

The pelletized blends were injection molded using a Custom Scientific Instruments Mini-Max molder. The sample cup was heated to 180°C, and about 1 g of pellets was placed in the cup. The rotor was lowered and the sample was mixed for a few seconds. Sample was manually injected into the mold by opening the bottom valve and applying pressure to the rotor. The mold was opened and the sample removed.

3.5 Blend Characterization

3.5.1 Scanning Electron Microscopy

The morphology of the polymer blends was examined by scanning electron microscopy (SEM). The compression-molded discs were fractured into bars approximately 5 mm wide. A bar was cut cross-wise with a razor blade at room
temperature. The samples were then placed in distilled water to dissolve out the water-soluble biopolymer phase. After 24 hours, the water was changed. After 48 hours the samples were drained, blotted, and placed in a vacuum oven at 50°C for 48 hours.

The extracted samples were mounted cut face up on a sample holder with silver paint and sputter-coated with a layer of gold-palladium alloy. They were examined in the AMR-900 scanning-electron microscope located in the T.M. Brooks Forest Products Research Center, with the assistance of Carlyle Price.

3.5.2 Transmission Electron Microscopy

Microtomed specimens were cut from compression-molded discs and mounted on grids by Steve McCartney of Materials Engineering. The samples were then stained by exposure to ruthenium oxide vapor for 30 minutes.

The samples were examined in the Phillips EM-60 electron microscope in the transmission mode.
4.0 MELT BEHAVIOR OF XYLAN DERIVATIVES

This chapter covers a study of the melt behavior of xylan esters and ethers. This was to demonstrate a relationship between the level and type of substituent and the melt behavior of the thermoplastic derivatives. It is shown that, while the various esters all exhibit distinct Tg values, thermoplastic flow is not observed. For the ethers tested, the flow properties are related to the degree of substitution, and to the bulk of the substituent group.

4.1 Materials

All of the derivatives in this study were prepared from a xylose-rich pentosan as described in section 3.1.

4.2 Characterization Methods

Chemical analysis of the derivatives was done to determine molecular weight, degree of substitution and glass transition temperature as described in section 3.3.

The melt flow properties of the material were screened using the flow test described in section 3.3.4.
Melt viscosity was measured for those materials which did flow, using the method described in section 3.3.5.

4.3 Results and Discussion

Figure 4 depicts the chemical structure of various substituents used to modify the xylan. Table III summarizes the derivatives prepared, and the results of the chemical and thermal characterization.

While the various esters were straightforward to prepare, and all exhibit T_g's when scanned by DSC (Figure 5), none of them flow under heat and pressure. The reason for this is not clear. No evidence of crystallinity or crystallization was observed by DSC. The broad glass transition typical of biopolymers was followed at higher temperature by an exotherm above 280°C attributed to the onset of thermal degradation. At the high temperatures the DSC sample head was fouled by volatile products condensing on the apparatus, further indicating degradation rather than crystallization. It is possible that the presence of a few glucuronic acid side chains is sufficient to provide enough dipole interactions between chains to inhibit flow; this phenomenon has been observed with synthetic polyesters (54). It is worth noting that
Figure 4. Chemistry of Xylan derivatives prepared.
Table III. Xylan Derivatives prepared and tested.

<table>
<thead>
<tr>
<th>Derivative</th>
<th>DS&lt;sup&gt;1&lt;/sup&gt;</th>
<th>Tg&lt;sup&gt;2&lt;/sup&gt;</th>
<th>flow?&lt;sup&gt;3&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>unmodified xylan</td>
<td>0</td>
<td>none</td>
<td>no</td>
</tr>
<tr>
<td>xylan acetate</td>
<td>1.96</td>
<td>52.3</td>
<td>no</td>
</tr>
<tr>
<td>xylan propionate</td>
<td>1.81</td>
<td>38.0</td>
<td>no</td>
</tr>
<tr>
<td>xylan butyrate</td>
<td>1.72</td>
<td>20.8</td>
<td>no</td>
</tr>
<tr>
<td>xylan hexanoate</td>
<td>1.48</td>
<td>-12.5</td>
<td>no</td>
</tr>
<tr>
<td>hydroxypropyl-x-1</td>
<td>0.65</td>
<td>62.3</td>
<td>yes</td>
</tr>
<tr>
<td>hpx-2</td>
<td>0.30</td>
<td>59.0</td>
<td>no</td>
</tr>
<tr>
<td>hpx-3</td>
<td>0.85</td>
<td>65.0</td>
<td>yes</td>
</tr>
<tr>
<td>hpx-4</td>
<td>1.42</td>
<td>68.6</td>
<td>yes</td>
</tr>
<tr>
<td>hpx-5</td>
<td>1.6</td>
<td>70.1</td>
<td>yes</td>
</tr>
<tr>
<td>acet(hpx-4)</td>
<td>2.0/1.42</td>
<td>43.5</td>
<td>yes</td>
</tr>
<tr>
<td>prop(hpx-4)</td>
<td>2.0/1.42</td>
<td>29.1</td>
<td>yes</td>
</tr>
</tbody>
</table>

<sup>1</sup> determined by NMR as described in 3.3.2

<sup>2</sup> determined by DSC as described in 3.3.3

<sup>3</sup> determined as described in 3.3.4
Figure 5. Differential Scanning Calorimetry of xylan esters.
the esters show a linear relationship between the size of the substituent and the glass transition temperature (Figure 6).

The ether hydroxypropylxylan presents a different picture. When the degree of substitution is below a threshold value of approximately 0.4 to 0.5, the material is not thermoplastic. This could be due to residual crystallinity at low degree of substitution; however, crystalline melting or crystallization was not observed below the temperature of thermal decomposition by DSC. Above this substitution threshold, the material is thermoplastic, and the melt viscosity decreases with increasing substitution, as shown in Figure 7. It should be noted that the sample HPX-1, DS=0.65, was not available in sufficient quantities to be tested in the RMS. Generally the melt viscosity is an increasing function of molecular weight, but in this case the molecular weight increase due to higher substitution was not the controlling factor in melt viscosity. Rather, a decrease in intermolecular interactions seems to be the cause of the reduced viscosity. While the number of hydrogen-bonding groups has not been reduced, the site of many of the groups has been moved to the flexible side chain, rather than directly on the backbone. This results in an overall reduction in chain stiffness, reducing the
Figure 6. $T_g$ of xylan esters, compared by substituent size.
Figure 7. Melt viscosity of hydroxypropyl xylan of varying degree of substitution, at 190°C.
melt viscosity. This flexibilization does not appear to have affected the glass transition temperature, which actually increases slightly as the substitution increases. (Figure 8.)

While direct esterification of the xylan did not result in thermoplastic derivatives, esterification of the incompletely-substituted ether HPX-4, DS 1.42, resulted in further modification to the melt behavior. Figure 9 shows the melt viscosity curves for HPX-4, acetylated HPX-4, and propionated HPX-4. Clearly, increasing the bulk of the substituent decreases the melt viscosity. In this series, the bulky substituents also reduce the glass transition temperature as shown in Figure 10.

In summary, a number of xylan ethers and esters have been prepared. The xylan esters do not exhibit thermoplastic flow, although there is a linear relationship between the size of the ether substituent and the glass transition temperature observed by DSC. The xylan ether, hydroxypropylxylan (HPX), has been prepared at several different degrees of substitution. There is a threshold level of 0.4 to 0.5 DS which is the minimum substitution which will give a thermoplastic derivative. Beyond this threshold, the melt viscosity is further
Figure 8. Glass transition of hydroxypropyl xylan of varying degree of substitution.
Figure 9. Melt viscosity of HPX esters, at equal level but different bulk of substituent. Temperature is 190°C.
Figure 10. Glass transition of HPX esters at equivalent level but different bulk of substituent.
reduced by higher substitution. Additionally, if the HPX is further derivatized by esterification of the side-chain and remaining backbone hydroxyl functional sites, the melt viscosity is also reduced.
5.0 BLEND STUDIES

In the previous chapter, selective chemical modification was shown to be a means of manipulating the melt viscosity of xylan derivatives. It is desired to incorporate these thermoplastic polysaccharides in melt blends to utilize the rare combination of thermoplasticity and biodegradability in a polymeric material. Since biodegradability of a multi-phase material depends on continuity of the degradable phase (6,7), it is necessary to understand the conditions that control continuity.

5.1 Introduction

In general, for a two-phase dispersed blend, the lower-viscosity component tends to become the continuous phase when present in sufficient quantity. Sperling (5) formulated a generalized relationship for phase continuity of a two-phase blend. Initially, given small amounts of component A and large amounts of component B, A will disperse in B. As the relative amount of A is increased, at some composition there will be a phase
inversion where component A becomes the continuous phase. The actual composition at which this occurs depends in large amount on the relative viscosities of the two phases. Sperling proposed that phase inversion could be predicted by the relationship

$$\frac{\eta_A}{\eta_B} = \frac{\phi_A}{\phi_B} \quad (10)$$

where $\eta_A$ and $\eta_B$ are the zero-shear viscosities of the components and $\phi_A$ and $\phi_B$ are the volume fractions. This is a generalized relationship which does not account for processing conditions or interfacial factors. Miles (47) recognized this limitation and proposed that the relationship be modified to account for variation in viscosity ratio that occurs due to process conditions

$$\frac{\eta_A(\dot{\gamma})}{\eta_B(\dot{\gamma})} = \frac{\phi_A}{\phi_B} \quad (11)$$

where $\dot{\gamma}$ is the effective shear rate of the mixing process used. Miles used compositions predicted by this model to demonstrate that, at the composition of phase inversion, cocontinuous structures could be achieved. Viscosity ratios tested ranged from 1 to 3.

Recently Ho, et al. (55) have tested this predictive
scheme for the system polypropylene/ethylene-propylene rubber, for viscosity ratios from 1.2 to 4.9. They found that equation 10 yields acceptable predictions of phase inversion for this system, particularly for lower values of viscosity ratio (less than approximately 2). They suggest that, at higher viscosity ratios, the observed data are better fit by an empirical equation such as

$$\frac{\phi_a}{\phi_b} = 1.22 \left( \frac{\eta_a(\dot{\gamma})}{\eta_b(\dot{\gamma})} \right)^{0.29}$$

(12)

where the dependence of phase inversion composition on viscosity ratio is not first order, as previously held, but rather of a fractional order.

The present study was undertaken to determine the relationship between viscosity ratio, composition, and phase texture for blends of a thermoplastic polysaccharide and polystyrene. Of particular interest are those compositions near phase inversion, where the polysaccharide becomes a continuous phase. There are three models from the literature, described above, which will be tested against experimental data to determine which, if any, yields acceptable prediction of phase inversion for the system under investigation. This will lead to the design of xylan derivatives for applications
in biodegradable blends where phase inversion and phase continuity are important considerations.

5.2 Discussion of experiments

The materials used in this study included three commercial hydroxypropyl celluloses, and one hydroxypropyl xylan. These materials are detailed in section 3.1 and 3.2. Five commercial polystyrenes were used as blend components, and these are detailed in section 3.2.2.

A suitable temperature for melt-blending the polysaccharides with the polystyrene(PS) was determined by experimentation. At temperatures above 180°C, there was significant browning due to thermal degradation of the polysaccharide. The polysaccharide did remain water-soluble, suggesting that extensive crosslinking was not a concern. Therefore 180°C was chosen as the processing temperature. Once this had been determined, the polymers were individually characterized by dynamic viscosity measurements as detailed in section 3.3.5. With four biopolymers and five polystyrenes, there were 20 possible combinations for binary blends. The viscosity ratio was calculated for each combination. This ratio, like the viscosity, is a function of shear rate. Since the mixing
The device used is the CSI-194 normal stress extruder, the actual shear rate of the process varies as the material is extruded, from a maximum at the outer edge to zero at the center outlet. Given the geometry of the extruder (20 mm diameter plates, 1.5 mm gap, 70 RPM), the maximum shear rate can be estimated to be 46 sec\(^{-1}\) by use of the relationship (56)

\[
\dot{\gamma}(R) = \frac{Q}{R} R \frac{R}{H} \quad (13)
\]

where \(Q\) is the angular velocity (2\(\pi\) x 70 rad/min), \(R\) is the radius (10 mm) and \(H\) is the gap (1.5 mm). When selecting blend combinations it was necessary to consider the range of viscosity ratios as well as the shear-rate dependence of each ratio. Table IV shows all the possible combinations, and the viscosity ratio at 21 sec\(^{-1}\), which was somewhat arbitrarily chosen as a reference shear rate, in the middle of the range of shear rates (0 - 46 sec\(^{-1}\)) encountered in the extruder.

Figure 11 shows the viscosity ratios of the six combinations chosen for study. It should be noted that the viscosity ratios vary slightly with shear rate, but the relative order remains the same with the exception of the xylan derivative combination. These combinations
Table IV. Blend combinations and viscosity ratios.

<table>
<thead>
<tr>
<th>Biopolymer</th>
<th>PS1</th>
<th>PS2</th>
<th>PS3</th>
<th>PS4</th>
<th>PS5</th>
</tr>
</thead>
<tbody>
<tr>
<td>HPC-G</td>
<td>0.42</td>
<td>0.52</td>
<td>0.38</td>
<td>0.39</td>
<td>0.33</td>
</tr>
<tr>
<td>HPC-H</td>
<td>0.11</td>
<td>0.14</td>
<td>0.10</td>
<td>0.10</td>
<td>0.09</td>
</tr>
<tr>
<td>HPC-L</td>
<td>0.08</td>
<td>0.10</td>
<td>0.07</td>
<td>0.08</td>
<td>0.06</td>
</tr>
<tr>
<td>HPX-5</td>
<td>0.44</td>
<td>0.55</td>
<td>0.40</td>
<td>0.41</td>
<td>0.35</td>
</tr>
</tbody>
</table>

1 $\eta$ biopolymer / $\eta$ polystyrene at 21 sec$^{-1}$ and 130°C.
Figure 11. Viscosity ratios of samples chosen for study. Temperature is 180°C.
cover the range of ratios from 0.08 to 0.55 (at 21 sec\(^{-1}\)).

The definition of viscosity ratio in this study is the biopolymer viscosity divided by the polystyrene viscosity, in every case. In the literature several definitions are used. Those researchers concerned with deformation and break-up of dispersed components, dating back to Taylor (38,39), have used \( \eta_{\text{dispersed}}/\eta_{\text{matrix}} \) as the definition. This definition allows ratios to vary from zero to infinity, but breaks down when the composition approaches phase inversion. Several current investigators (47,55) have used the ratio of the higher-viscosity component/lower-viscosity component, which allows ratios to vary from one to infinity. In the present study all ratios are defined as the ratio of biopolymer viscosity/polystyrene viscosity.

As discussed earlier, this study will compare experimental results to three models from the literature for the relationship between viscosity ratio and the composition of phase inversion. Figure 12 shows the predicted compositions of phase inversion for the polysaccharide-polystyrene system under investigation, as predicted by the three models. Volume fractions have been converted to weight percents using the following specific
1 viscosity ratio defined as ratio of shear-dependent viscosities.

2 viscosity ratio defined as ratio of low-shear viscosities.

Figure 12. Predicted composition of phase inversion. Predictions of Sperling (reference 5), Miles (reference 47) and Ho (reference 55).
volumes at 180°C calculated from room-temperature densities and thermal expansion coefficients given in reference 53: polystyrene 1.06 ml/g; hydroxypropyl cellulose 0.892 ml/g. Hydroxypropyl xylan was assumed to be similar to hydroxypropyl cellulose.

Thus the results of an experimental study of phase inversion versus composition and viscosity ratio can be compared with the predicted results from the models to determine which if any model(s) provide acceptable predictions for this system.

5.3 Results and Discussion

Samples were made of each combination at 0, 10, 20, and 40 weight percent. At 40 percent, the blends were difficult to extrude, as the extrudate strand broke frequently even under minimal tension, and the extruder output was erratic. In the case of 40% HPX in PS2, the blend did not extrude at all. These extrusion limitations are discussed below. After extrusion, the blends were compression-molded into discs and fractured for SEM examination. Figures 18 through 23 show the micrographs for the series, in order of increasing viscosity ratio. At composition of 20 percent, the biopolymer phase, which was dissolved prior to examination, appears as discrete inclusions whereas at 40 percent there is a suggestion of
Figure 18. Scanning-electron micrograph of blends of HPC-L and PS1, 2000X. a) 0 wt.% HPC. b) 10 wt.% HPC. c) 20 wt.% HPC. d) 40 wt.% HPC. Approximate viscosity ratio of this combination is 0.08.
Figure 19. Scanning-electron micrograph of blends of HPC-H and PS2, 2000X. a) 0 wt.% HPC. b) 10 wt.% HPC. c) 20 wt.% HPC. d) 40 wt.% HPC. Approximate viscosity ratio of this combination is 0.15.
Figure 20. Scanning-electron micrograph of blends of HPC-G and PS5, 2000X. a) 0 wt.% HPC. b) 10 wt.% HPC. c) 20 wt.% HPC. d) 40 wt.% HPC. Approximate viscosity ratio of this combination is 0.35.
Figure 21. Scanning-electron micrograph of blends of HPC-G and PS3, 2000X. a) 0 wt.% HPC. b) 10 wt.% HPC. c) 20 wt.% HPC. d) 40 wt.% HPC. Approximate viscosity ratio of this combination is 0.4.
Figure 22. Scanning-electron micrograph of blends of HPC-G and PS2, 2000X. a) 0 wt.% HPC. b) 10 wt.% HPC. c) 20 wt.% HPC. d) 40 wt.% HPC. Approximate viscosity ratio of this combination is 0.55.
Figure 23. Scanning-electron micrograph of blends of HPX-5 and PS2, 2000X. a) 0 wt.% HPC. b) 10 wt.% HPC. c) 20 wt.% HPC. d) 40 wt. % was not possible. Approximate viscosity ratio of this combination varies with shear rate.
continuity between the biopolymer domains, for every blend.

The samples of 40 percent biopolymer were further examined by transmission-electron microscopy. The specimens were microtomed into ethanol rather than water because of the water solubility of the biopolymer. In most places the biopolymer phase fell out of the thin section when the sample was microtomed, due apparently to a lack of interfacial adhesion between the components. Therefore the size and shape of the biopolymer phase is evidenced by the holes in the section. Figure 24 shows the TEM of two blends, HPC-H in PS2 and HPC-G in PS2, both at 40% biopolymer. These represent viscosity ratios of 0.11 and 0.53. While the SEM evidence suggests continuity of the biopolymer phase, the TEM clearly shows that the biopolymer is a dispersed phase. It is interesting to note that the lower viscosity ratio has smaller droplet size and thus a finer texture. This agrees with the results of Wu (44) who found that, with all other factors equal, lower viscosity ratios will lead to smaller dispersed particles in compositions where one component is present as a dispersed phase.
Figure 24. Transmission-electron micrograph of two blends. 
a) 40 wt.% HPC-H in PS2, approx. viscosity ratio of this blend at 180 °C is 0.15. 
b) 40 wt.% HPC-G in PS2, approx. viscosity ratio of this blend at 180 °C is 0.55.
No phase inversion was observed for any of the experimental samples, in direct contradiction of the predictions of Sperling and Miles. Table V shows the experimental samples, the predicted, and experimental compositions of phase inversion. While the experiments indicate a lack of compliance with Sperling and Miles, the results are consistent with the model of Ho. Compositions of phase inversion were not reached due to extrusion limitations, and thus a complete test of Ho's model for this system was not accomplished.

Ho's model represents an evolution of Miles and Sperling. It is not designed to be applicable to different types of systems, or different ranges of viscosity ratios than the earlier models, but rather is an empirical correction which better fits observed phase inversion data than the uncorrected models. This correction appears to be applicable to the system under investigation, as the experimental results comply with Ho's predictions over the range tested. Indeed, the lack of variation in texture as viscosity ratio is altered in this study seems to indicate a dependence on viscosity ratio that is less than expected from the earlier models, and the major difference in Ho's model is a fractional rather than first-order dependence on viscosity ratio.
Table V. Combinations studied and compositions of phase inversion.

<table>
<thead>
<tr>
<th>Combination</th>
<th>Predicted phase inversion</th>
<th>observed</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>weight percent biopolymer</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sperling(^1)</td>
<td>Miles(^2)</td>
</tr>
<tr>
<td>HPC-L - PS1</td>
<td>13%</td>
<td>9%</td>
</tr>
<tr>
<td>HPC-H - PS2</td>
<td>28%</td>
<td>12%</td>
</tr>
<tr>
<td>HPC-G - PS5</td>
<td>32%</td>
<td>28%</td>
</tr>
<tr>
<td>HPC-G - PS3</td>
<td>47%</td>
<td>31%</td>
</tr>
<tr>
<td>HPC-G - PS2</td>
<td>50%</td>
<td>38%</td>
</tr>
<tr>
<td>HPX-5 - PS2</td>
<td>29%</td>
<td>39%</td>
</tr>
</tbody>
</table>

\(^1\) Reference 5. These are calculated using viscosity ratio at low (1 sec\(^{-1}\)) shear rate.

\(^2\) Reference 47. These are calculated using viscosity ratio at 21 sec\(^{-1}\) shear rate.

\(^3\) Reference 55. These are calculated using viscosity ratio at 21 sec\(^{-1}\) shear rate.

\(^4\) determined experimentally by SEM and TEM.
A quantitative comparison of predicted versus observed composition of phase inversion is obviously not possible due to the lack of observed phase inversions over the range of compositions tested. The range of compositions was limited by the extrusion process; above 40 percent HPC the blends simply would not extrude from the extruder. The CSI extruder is a normal stress extruder; melt is pumped through the die by the pressure gradient that exists as a result of normal stresses generated when the melt is sheared. These normal stresses reflect the elastic behavior of non-Newtonian fluids such as polymer melts. A Newtonian fluid, which lacks normal stresses, would actually flow backward through the extruder due to the centrifugal forces generated by the rotation. Erratic flow, or no flow, through the extruder might be related to the magnitude of the normal stresses in the melt.

To test this possibility, the viscoelastic data on each blend was examined. It might be anticipated that, if low normal stresses are the cause of extrusion limitations, the blends which became increasingly difficult and ultimately impossible to extrude as the biopolymer content was increased would show decreasing normal stresses as the biopolymer content was increased. The normal stresses are a measure of elasticity, and thus
are reflected in the magnitude of $G'$. The primary normal stress difference ($N_1$) of a melt can be approximated (51,52) as $2G'$ at low to moderate shear rates up to several hundred seconds$^{-1}$. Figure 25 a-f shows $N_1$ for each of the blend combinations, at varied compositions, at 21 sec$^{-1}$. Clearly $N_1$ for the pure biopolymers are lower than for the polystyrene in each case. $N_1$ generally drops off with increasing biopolymer content, which could account for the extrusion problems. Furthermore, the lowest $N_1$ values occur for combination a., HPC-L in PS1. This was the combination which was the most difficult to extrude at 40 weight percent, except for HPX-5 in PS2 which did not extrude at all.

The normal stresses do not appear to follow a consistent pattern with respect to composition. Combinations a., d., and f. appear to show s-shaped curves in which the initial portion of the curve is concave downward. Combination c. appears as an s-shaped curve in which the initial portion of the curve is concave upward. Combinations b. and e. do not appear to follow any pattern. There is no general pattern for this series, which is unexpected because the blends differ primarily in the molecular weights of the components and thus might be
Figure 25. Primary normal stress difference $N_1$ for blends tested. a) HPC-L in PS1. b) HPC-H in PS2. c) HPC-G in PS5. d) HPC-G in PS3. e) HPC-G in PS2. f) HPX-5 in PS2.
expected to follow the same general pattern. However, this is not what is observed. Inconsistencies and scatter in blend data have been attributed to poor dispersion (46). While the electron micrographs show locally good dispersion, the extrusion problems and scattered rheological data suggest that the blends are not completely well mixed. This concern could be eliminated by using a different mixing device such as a batch mixer where mixing time could be increased to achieve better mixing.

Another potential reason for the scattered rheological behavior could be thermotropic behavior of the HPC. The deformation and breakup of the HPC is controlled by the viscosity ratio as described earlier. Thermotropic behavior would impact the texture of a blend only to the extent that it affected the melt viscosity; however, this behavior could have a big effect on the normal stresses in the melt. Liquid-crystalline polymers have been shown to have complex normal-stress behavior, including in a few cases negative normal stresses (57) which are unheard of in any other type of polymer. Thus the scattered normal-stress behavior observed might be a result of liquid-crystalline behavior of the HPC. In any case, the normal stress behavior of the blends is indicative of a complex
rheological behavior which could account for the extrusion problems encountered with these blends in a normal-stress extruder.

In summary, a series of blends were prepared, with varying viscosity ratio and composition. The blends were examined by scanning-electron microscopy. The texture of the blends did not appear to be affected by viscosity ratio, but the composition had a pronounced effect on texture. Compositions of phase inversion could not be achieved due to extrusion limitations which appear to be related to normal stresses. Phase inversions were not seen in the composition ranges predicted by Miles (47). The model of Ho (55) predicts phase inversion at compositions higher than those tested and thus this model is not contradicted by the observed results.
6.0 CONCLUSIONS AND RECOMMENDATION

Based on the results of these studies, the following conclusions can be drawn:

1. Xylan can be chemically modified to give thermoplastic derivatives.

2. The melt viscosity of the xylan derivatives is a function of the level and type of substituent. There is a threshold level of substitution which must be achieved before a derivative is thermoplastic. Above this threshold, increasing the level of substituent decreases the melt viscosity.

3. Substituents with higher molecular weight reduce the viscosity more than similar substituents with lower molecular weight.

4. Viscosity ratio is not the controlling factor for texturing of hydroxypropylcellulose-polystyrene blends over the range of ratios $0.08 < \text{VR} < 0.6$. The texture could be varied by altering composition. This finding contradicts the models of Sperling and Miles. It is consistent with, but does not validate, the model of Ho.
The following recommendation is made for continued research:

1. This set of experiments utilized a single xylose-rich pentosan as the base material for modification. Continuing research on isolation and purification methods has resulted in pentosans of varied molecular weights and higher purity than the sample used herein. Varying molecular weight and molecular weight distribution is a common method used by manufacturers to tailor the melt flow characteristics of synthetic polymers. A further study of melt flow characteristics of xylan derivatives should focus on the impact of molecular weight on melt viscosity for derivatives of the same type and level of substituent. This would be accomplished by using base xylans which differ in molecular weight, and chemically modifying them to desired derivatives which would then be tested in the same manner as the derivatives in this work.

Based on personal experience with the experimental methods used in this study, the author offers the following advice and suggestions for researchers who wish to follow this work:
1. Hydroxypropyl cellulose was used in Chapter 5 as an analog for hydroxypropyl xylan. However, the melt flow behavior of the HPC and HPX is sufficiently different to raise questions as to the validity of using HPC. In particular, the HPC shear-thins faster and has a lower melt viscosity at moderate shear rates (50-500 sec\(^{-1}\)) than the HPX of lower molecular weight (recall Figure 11). It is suspected that this is due to the thermotropic nature of HPC at 180\(^\circ\)C. To avoid these questions it is recommended that future studies use pentosan derivatives of varied melt viscosity, rather than some pentosan and some hexosan (cellulose) derivatives. The melt viscosity of pentosan derivatives can be modified by varying the level and type of substituent as shown, and possibly by varying the base pentosan (pending the results of the investigation proposed above).

2. A well-controlled mixing device, such as a twin-screw closed-chamber batch mixer should be used for further small-scale melt blending work. This type of device would allow for the mixing time to be controlled, and thus thorough mixing could be achieved. Also, this type of mixer is not as sensitive to the rheological properties of the polymers as the normal-stress extruder
used here, and thus a broader range of composition will be possible. This will allow a thorough testing of the various models for phase inversion, if desired.
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