Modification and Characterization of Starches and Starch-Based Blends for Use as Environmentally Biodegradable Thermoplastics

by

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Abstract

The use of starch in environmentally degradable thermoplastics is an attractive idea, due to the abundance of its natural sources as well as its natural biodegradability. This thesis studies different aspects of the utilization of starch for biodegradable thermoplastic applications, dealing mainly with physical and chemical modifications of starch for this purpose.

Irradiation-modification of the blends of various starches with a synthetic polymer (poly ethylene-co-vinyl alcohol) were carried out using an electron beam, and changes in the rheological, thermal and mechanical properties of the blends as well as in their microstructure were evaluated. The data indicate, consistent with other reports in literature, that starch molecules fragment under the effect of ionizing radiation, while the EVOH is relatively unaffected. These substantial (mainly physical) modifications to the starch molecules manifest themselves in changes in the rheological and thermal behavior of the blends. Furthermore, the mechanical properties of filaments obtained from molten irradiated pellets were quite different from those of control filaments. Micrographic examination of some blends indicated a correspondence between a modification in the microstructure of the filaments and a change in their mechanical properties. It seems likely that the enhanced mobility of the fragmented starch molecules in the melt is responsible for these changes in the microstructure and concomitantly, the mechanical properties of the blend. Such an irradiation-based physical modification of starch may be of use in tailoring the properties of commercial blends of starches with synthetic thermoplastics.

As a different route to starch-based thermoplastics, a series of fatty acid esters of high-amylose starches were prepared. The rheological, thermal, and mechanical properties of these starch esters (as well as the effects of adding plasticizer on some selected properties) were evaluated. Increasing ester length and increasing plasticizer contents make these starch-based materials more processable, and more ductile. Still, their applicability is likely to be limited by their properties and cost, especially in comparison to commodity thermoplastics. Blending of starch and starch esters was also attempted with some success.

Thesis Supervisor: Prof. Edward W. Merrill
Carbon P. Dubbs Professor of Chemical Engineering
Acknowledgments

*The time has come, the Walrus said, to speak of many things...*
How about some that made my life at MIT less harrowing!

They say that this is the most fun part of one's thesis. Hmm, does that imply that other parts are fun too? Anyway, let's see, who do I start with? Ah, your advisor, you say. Well, I think most people who will read this section already know of Prof. Merrill (especially those who gnashed their teeth at my crowing about the advisor who lets his students take real vacations), and his colorful analogies, i.e., the Cheshire cat meets waving seaweed on the ocean floor meets Maxwellian demons. Add to his encyclopedic knowledge of polymers an appreciation for things not plastic, and garnish with a wonderful sense of humor, and all in all, you have an inimitable experience for his students. Hah, hah, I was at MIT, and I had an advisor who treated me as a human. Feels great to beat the system...

I am grateful to Prof. Rose and Prof. Thomas, esteemed members of my thesis committee, for their advice, feedback, and support; I should also note that this section, and the others following it, may not have have been written if Bob hadn't encouraged me to join PPST all those eons ago. I would also like to thank Ken Wright for coaxing electrons out of the Van de Graaff generator for my benefit, and Prof. Armstrong for taking the time to discuss with me the finer points of the starch blend rheology.

Over the years, in all my different incarnations at MIT, I have had the good fortune of meeting a fair passel of peers, often eclectic, generally fun, and sometimes intelligent. From many I learned about polymers and science, from many I learned about life in general, and from some I learned nothing in particular (and that was probably the most fun). So, suppress your yawn, and move you on to read about some of these creatures...

I arrived in the Merrill lab (after a fun-filled year with my PPST cronies spent in relentless pursuit of academic excellence, as well as wine, women, and song, not necessarily in that order) a novice in the ways of real polymer science. I have to thank all the students in the lab for giving so freely of their time to advise me on all matters of lab technique in those halcyon days, especially Eliot with whom I worked closely in my first few months. But nothing in life is free, they say. So, of course I paid for all that expert advice in the form of constant ribbing and the merciless teasing. Stephanie, of course, was the most remorseless in that regard, that side of being hidden very well by her exterior sweet and helpful disposition (this facade serving her well in her telephone romance with Joe Sartorius). Chuck and Timoshenko certainly did not hold back with their invectives either, often leaving me speechless since I strongly believed that impoliteness is a cardinal sin. Luckily I eventually overcame my inhibitions and learned to give almost as well as I got. It was also great to glean travel tips from the consummate travellers in the lab, Deb and the aforementioned Timo, who elevated the art of blending vacation and work (concepts that often seem to have a very high free energy of mixing) to a heretofore unparalleled level. I also have to thank Alice for being a great first officemate, especially for her constant updates on the progress on the CDM Building. Too bad she wasn't here for Building 68! Even though I voluntarily forfeited the pleasure of supervising UROPs, the presence of 'genes and Yvette in the lab allowed me the delightful opportunity of meeting fun and intelligent children (yup, that's me saying that about MIT undergrads!). The time spent with this lab crew both at work and play, the 10.EWM seminars, the Whitehead lunches, the Tetris sessions, and the general bantering and socializing (aka BS) sessions etc. was indeed enjoyable.

Recent years have brought forth a new crop of students to the Merrill lab who have generally followed the historical pattern of treating the lab as a place for more than just
research. Sue, with whom I have shared many cursing sessions for a certain company on the West coast, and who has also been my partner in innumerable coffee breaks and sundry bull sessions, has been a wonderful officemate (when she is not blowing my hair back). In my various dealings and discussion with Ed in the lab, apart from other things, I have gained great insight into the philosophy of the medical profession, and the psyche of physicians. A recent addition to the lab fold, a fellow countryman who goes by the handle of Premi, has already shown a penchant for indulging in didactic discussions in a variety of issues, discussions which I have enjoyed immensely, as I'm sure will his wife someday. I am sure that this lab environment will continue to provide future grad students with as wonderful a time (though, hopefully for them, not as long) as I had here.

My merry band of friends from my earliest days at MIT, party animals all (yeah, right!), Rob, Bruce, and Tom receive due thanks for taking under their wing a stranger in a strange land a long time ago. I especially enjoyed those study sessions in the libraries where they attempted to convert me to workaholism through applications of immense peer-pressure; years have passed but the pressure has only intensified! Suffice it to say that I hope that their efforts in establishing careers are more successful. I also have to thank Rob, my eventual roommate, for allowing me an up-close glimpse into American living, including cuisine of a kind that I had never tasted before. Véronique, though a late arrival to this group (thanks to a timely introduction by Richard, my erstwhile tennis partner ever gracious in defeat), certainly perked us up socially, and me in innumerable other ways as well. Recently, this social group has also included Brian and Dan (physicists, you know: if there was anything more interesting, they would be doing it!), my cohorts on one of those interminable journeys from Hopkinton.

During the period when my research seemed to be in limbo, I had the luck of meeting up with a set of very stimulating TPP students with whom I spent a good many days and evenings indulging in all kinds of social activities that often degenerated into late-night debates about weighty matters of all manners. (I do like to debate on occasion, as my friends will attest to.) I have especially enjoyed the times spent with Seab, Lord of Sloth (oh, what an utterly dreadful concept) and Chris the Diligent (methinks thou dost protest thy Anglophileness too much). I also maintain fond memories of my immersions into South American culture, courtesy of Marcelo and Veronica, with those delectable Argentinian dinners and the inevitable postprandial discussions.

While at MIT, I have always found my peers to be of great help, but it is especially during my finishing throes that everybody around me has been extremely helpful in extending their expertise and other help to me. For this, I would like to especially acknowledge Marcelo who was instrumental in the collaboration on the irradiation studies, Bruce for his constant feedback and help, particularly on light scattering, Ramnath for help in mechanical testing and DMA, Véronique and Andreas for allowing generous use of their computers and printers, and Brian for his machining tutelage and the eventual loan of his printer. I would also like to thank Mike Frongiolo for allowing me to avail of his expertise on the ESEM.

In the end, my biggest thanks go to Véronique and to my family. Véronique, a wonderful friend and companion, has constantly encouraged me, listened to my laments, and borne my mercurial temperament with good humor over the years. My parents and siblings have been a source of unremitting and unquestioning support on my long and winding journey, as well as the catalysts for much critical self-assessment. I am where I am mainly because of my family, and I know wherever I will end up, I will have all their encouragement and love. And Papa and Mummy, now that I'm done, can I go and play?

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Chapter 1: Introduction

The adverse environmental impacts of disposing solid wastes have become increasingly apparent in the last few decades. This, coupled with the projected sharp decline in landfill availability, has resulted in a greater emphasis being placed on issues relating to solid waste generation and disposal. Among the various materials that comprise solid wastes, polymers have been the focus of much attention for a number of reasons. Their use has been increasing rapidly; plastics were estimated to comprise (by weight) 2.7%, and 7.3% of the municipal solid wastes (MSW) in 1970 and 1986 respectively (OTA 1989). They also occupy a disproportionately high volume for a given weight compared to other materials; thus, 1986 estimates attributed approximately 20% of the MSW volume to plastics (OTA 1989). And, perhaps the most important, most plastics have been designed for stability in the environment, and are therefore generally non-degradable. Ingestion of plastic waste by wildlife, and ensnarement of small animals by objects such as six-pack rings have been the cause of significant concern among environmentalists. This has resulted in regulation concerning aspects of plastics disposal at both the national and international level, of which a particularity notable one is Annex V of the international treaty MARPOL 73/78 which prohibits the dumping of all non-degradable plastic waste at sea.

Among the various strategies to ameliorate the problems related to plastic disposal, a promising one (at least for some specific applications) is the use of plastics that degrade in the natural environment. There are a number of different approaches to environmentally degradable thermoplastics (Lenz 1993, Swift 1993). It is possible to introduce

† The United States Environmental Protection Agency has estimated that, by the year 2006, the number of landfills in the U.S. is expected to decline by 80% of the 1986 levels (OTA 1989)
degradability into certain synthetic polymers through chemical modification routes such as introducing linkages in the carbon backbone that make it susceptible to hydrolysis or photodegradation. A well-known commercial example of this approach is the incorporation of carbon monoxide in polyethylene to yield main-chain carbonyl linkages that are susceptible to scission under ultraviolet light (Scott 1973). In recent years, other sophisticated modification routes have also resulted in the development of other degradable polymers such as those with ester groups inserted into carbon-chain polymers (Bailey 1983). Unfortunately, such chemistry-based approaches generally add complexity to the synthesis procedures, which can ultimately adversely affect the economics of production in a significant manner.

A completely different approach, and one that has been receiving significant attention, is to use natural polymers either by themselves or as components of thermoplastic blends, using the fact that molecules of biological origin will eventually degrade in the environment under the action of microorganisms. A limited number of biopolymers (mainly bacterial polyesters) offer by themselves a combination of thermoplastic processability and suitable physical properties for commercial applications, although generally their widespread use has been hampered by unfavorable economics. Even though many other natural polymers may not exhibit physico-chemical properties that allow them to be used by themselves (at least in an unmodified form) as commodity thermoplastics, these are still very attractive as potential candidates for components of biodegradable thermoplastics because of their low cost and ease of availability. Starches, a class of natural polysaccharides produced by most plants as a method for storing energy, belong to the latter category, and have been the specific focus of much attention due to an abundance of feedstocks from agricultural crop sources in the United States.
Starch is essentially a glucosidic polymer, with a mainly linear component (amylose) that consists of \( \alpha-(1 \rightarrow 4) \) linkages between the glucose rings, and a highly branched component (amylopectin) that consists of \( \alpha-(1 \rightarrow 4) \) and \( \alpha-(1 \rightarrow 6) \) linkages, the latter serving as branch points. Figure 1.1 shows the general structure of the amylose and amylopectin components. Although the detailed fine structure of amylopectin is still a matter of on-going discussion, Figure 1.2 illustrates the general model of amylopectin proposed by Robin et al. (1975) that has received acceptance in recent years (Blanshard 1987). The starch polysaccharides are sizeable molecules: generally amylose molecules have molecular weights in the range of \( 10^5 \) - \( 10^6 \) daltons and the much larger amylopectin molecules have molecular weights exceeding \( 10^7 \) daltons and often even greater than \( 10^8 \) daltons (see Table 1.1) (Young 1984). It has also been shown that some starches, especially the high-amylose maize varieties, contain significant amounts of material with properties intermediate to amylose and amylopectin. This has been identified as amylose with some long-chain branching.

In the plant, the starch molecules are synthesized within granules. The relative fractions of these two components, and their distribution within the granule can vary significantly depending upon the source of the starch. In the granule, the amylopectin molecules are arranged in the radial direction, with the short branches being packed in an ordered fashion, presumably as the molecules are synthesized. It is this packing arrangement that is responsible for the crystallinity in the granule. The amorphous regions within the granules are occupied mainly by the amylose molecules, although some parts of the amylopectin molecules also lie within these domains and amylose molecules are also present in the crystalline domains. The positions of the various molecules, and their interactions within starch crystallites is shown in Figure 1.3 (Blanshard 1987). As a consequence of the mostly amorphous nature of the amylose, it can be leached out with
Table 1.1: Molecular weights of amylose and amylopectin from various sources, measured by light scattering (from Young 1984).

<table>
<thead>
<tr>
<th>Source</th>
<th>Amylose (10^6 daltons)</th>
<th>Amylopectin (10^6 daltons)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rubber Seed</td>
<td>(0.24)</td>
<td></td>
</tr>
<tr>
<td>Sweet Corn (Z. mays)</td>
<td>(0.18)</td>
<td></td>
</tr>
<tr>
<td>Potato</td>
<td>1.9, (0.49)</td>
<td>440, 65</td>
</tr>
<tr>
<td>Wheat</td>
<td>1.33, 2.65, (0.34)</td>
<td>400</td>
</tr>
<tr>
<td>Barley</td>
<td>2.11</td>
<td>400</td>
</tr>
<tr>
<td>Oat</td>
<td>2.19</td>
<td></td>
</tr>
<tr>
<td>Rye</td>
<td>2.50</td>
<td></td>
</tr>
<tr>
<td>Smooth Pea</td>
<td></td>
<td>500</td>
</tr>
<tr>
<td>Wrinkled Pea</td>
<td></td>
<td>500</td>
</tr>
<tr>
<td>Tapioca</td>
<td></td>
<td>450</td>
</tr>
<tr>
<td>Waxy Maize</td>
<td></td>
<td>400</td>
</tr>
</tbody>
</table>

* Data in parentheses are for amylose fractionated by anaerobic fractionation; the rest of the data are for solutions prepared in dimethyl sulfoxide.

relative ease without disrupting the overall structure or crystallinity of the granule. Once in solution, amylose molecules have a tendency to crystallize ("retrograde"); the presence of strong hydrogen bond disrupters such as urea, alkalis, or dimethyl sulfoxide helps maintain these molecules in solution by preventing their association. Although a significant research effort has been devoted to the molecular structure as well as the solid state and
solution behavior of starch and its components for over fifty years now, a complete understanding has been stymied by the extremely complex nature of these molecules.

Overall, this heterogeneous granular structure adds great complexity to the behavior of starch during its processing. Mechanical and thermal forces, in conjunction with the presence of water or other plasticizers can have a variety of effects on the starch granules, all the way from simple granular rupture to extensive gelatinization and molecular fragmentation (Lai and Kokini 1991). Such structural changes in starch are likely to have important ramifications for the eventual properties of the processed starches or starch-containing materials.

The utilization of starch in different forms as the basis or components of engineering materials has been the source of speculation and research for many decades now. In the 1940s and 1950s, a significant research effort by many workers focused on starches and its derivatives. Although it was possible to prepare self-supporting films of pure starch or its components, their mechanical properties (especially in terms of ductility and toughness) left much to be desired. All in all, the pure components of starch were found to be clearly unsuitable for applications requiring mechanical strength.

In about the same period, a significant amount of work was also carried out to explore the potential of starch esters to replace cellulose-based thermoplastics such as cellulose acetate and cellulose acetate-butyrate. Cellulose, a first cousin of starch, is chemically identical to the latter, but utilizes a $\beta-(1\rightarrow 4)$ linkage between the glucan units. Although such a difference in the molecules seems minor, it results in a very different character in the two polysaccharides: cellulose is a structural polymer, and starch serves the function of energy storage in plants. Presumably for this reason, derivatives of even purified amylose materials were found to consistently have properties inferior to their cellulose counterparts. Consequently, interest in industrial thermoplastic applications of
starch dwindled until the mid 1970's when blending of starch with thermoplastics began to be explored. However, as mentioned earlier, it is the recent environmental movement that has provided the strongest impetus for renewed research in starch applications for commodity thermoplastics.

This thesis covers various aspects of starch technology that might be of potential use for thermoplastic applications as well as some related basic scientific inquiries in this context.† Chapter 2 deals with a study of blends of starch with synthetic thermoplastics, and the effects of irradiation-based physical modification of the starch on various solid-state and melt properties of the blends. Chapter 3 is a study of fatty acid esters of starch, once again in terms of their solid and melt properties. Also explored, very briefly, is a combination of the two ideas, in a sense: i.e., the blending of thermoplastic starch esters with the unmodified starches. Chapter 4 draws some general conclusions from this research, and briefly lays out possible directions for future explorations along these lines. Some aspects of the molecular characterization of starches (with special reference to the effects of extrusion processing upon the size and structure of the starch polymers) which are not of direct consequence to the main work presented in this thesis are appended at the end.

† This work was part of a broad research effort sponsored by the USDA to develop starch-based environmentally degradable thermoplastics. The focus of the research groups at MIT involved in this effort has been on various, inter-related aspects of the polymer science underlying such a use of starch. At the time of the writing of this thesis, detailed studies on the morphology of the starch-containing blends (same as the control blends referred to in Ch. 2 in this thesis) are being carried out by S. Simmons, and their rheology is being studied by D. Lee.
Fig. 1.1: General structures of the components of starch: (a) Amylose, (b) Amylopectin
Fig. 1.2: Structure of amylopectin according to the model of Robin et al., 1975 (from Blanshard 1987).
Fig. 1.3: Model of the crystalline domain of the starch granule (from Blanshard 1987).
2.1 Introduction

Although a number of different approaches have been attempted to commercially utilize starch for biodegradable plastics applications, almost all have involved compounding starches in some form with synthetic thermoplastics. The most common (and one of the simplest) of these involves compounding of native, unmodified starch with autooxidant-containing polyethylene whereby the starch acts as a granular filler, and serves to enhance the free-radical-based degradation of the synthetic polymer (Griffin 1974, 1977a,b; Maddever and Chapman 1989). Another route that has been explored is the blending of gelatinized, modified, or plasticized starch with synthetic polymers such as polyvinyl chloride (Westhoff 1974), as well as poly(ethylene-co-acrylic acid) and polyethylene (Otey 1977, 1980, 1987). Some subsequent research efforts have exposed newer formulations consisting of blends of starch with other synthetic polymers such as poly(caprolactone) ((Tokiwa et al. 1991), or natural polymers such as poly(hydroxy alkanoates) (Ramsay 1993).

One common feature of all these various processes is that the starch does not really melt under these conditions of compounding (since the melting point of native starch is higher than the blending temperatures). The fact that high concentrations of plasticizers can significantly depress the melting and glass transition point of starch under high pressure and allow it to be processed like a thermoplastic has been the basis of newer processing procedures developed in the last few years (Tomka et al. 1987a, b). Unfortunately, even though pure starch can be melt-processed under these specific conditions, it is still unusable by itself for most end-applications because of its generally unsatisfactory
mechanical properties, and their dependence upon the starch water content (which in turn can vary greatly with the ambient conditions). Consequently, successful commercial use of thermoplastically-processed starch still requires blending with other degradable polymers that lend acceptable mechanical and physical properties to the blend. Examples of biodegradable synthetic polymers that have been explored for thermoplastic blending with starch include poly (vinyl alcohol) (Otey 1974, Nwufo and Griffin 1985) and poly (ethylene-co-vinyl alcohol) (George et al. 1994).

Although the blending of starch with thermoplastic materials has been attempted in various forms mentioned here over the last two decades, it is only recently that the inter-relationships between the processing parameters, the morphology and the properties of such blends are beginning to be studied in a systematic manner (e.g., Simmons et al. 1993). Generally, it is seen that the addition of starch to thermoplastics has adverse effects on the mechanical properties, as evident from a lowering of the ultimate tensile strain and stress values for these blends as compared to the neat thermoplastics (e.g., Ramsay 1993). Some reports in the literature indicate that the physical and mechanical properties of starch-containing plastics can be favorably modified by chemical modification of the starch previous to the blending. This has included surface modification of the starch granules (Evangelista 1991) as well as modification at the molecular level (Swanson 1988). Such a modification of properties is presumably due to changes in the interactions between the (chemically modified) starch and the thermoplastic with which it is blended, and hence changes in the morphology of the blend. However, the mechanisms underlying these property modifications do not seem to be completely clear, especially since the morphology of starch-containing blends has generally been studied only to a limited extent by techniques such as scanning electron microscopy. Still, these observations highlight the importance of studying the interactions at the molecular level between the starch and the
blending thermoplastic, their relationship to the processing and the eventual structure of these blends, and the implications therein for the physical-mechanical properties of such composites.

The aim of the current work was to study the effect of molecular modification of starches on their blends with thermoplastics. In contrast to most of the previous studies reported in literature, our objective was to attempt to impart significant structural modifications to the starch molecules without significantly altering its chemical structure. In the present study, starch modification was carried out by means of electron-beam irradiation of a series of blends of starch and poly(ethylene-co-vinyl alcohol). Following this, the rheological and mechanical properties of these blends were studied over a range of starch-synthetic polymer compositions, for different kinds of starches. Brief studies were also carried out on the morphology and other physical characteristics of these blends in order to understand the relationships between the radiation modification of these blend materials and its effect on their processing, morphology and mechanical properties.

2.2 Experimental

Three different kinds of corn starch (National Starch Co.) were utilized in this study, differing essentially in their relative fractions of amylose and amylopectin: a waxy maize starch (Amioca), essentially 100% amylopectin, a native corn starch (Melojel), approximately 70% amylopectin and 30% amylose, and an acid-modified high-amylose starch (EK Fl. Hylon VII), approximate amylopectin content 30%, and amylose content 70%. These are subsequently referred to as WM, NC, and HY, respectively. The other major component of the blends, the synthetic polymer, was a random copolymer of ethylene and vinyl alcohol, namely poly(ethylene-co-vinyl alcohol) (Eval Corp., EVAL
E105A), 44 mol % ethylene, and number- and weight-average molecular weights of about 50,000 and 100,000 respectively, referred to as EVOH in this chapter.

2.2.1 Blend Preparation

The compounding of the blends was carried out using a 34 mm co-rotating twin-screw extruder (Leistritz) at the Novon division of the Warner Lambert Corporation. The dry feed to the extruder consisted of a mixture of starch powder and EVOH pellets (conditioned at 50% relative humidity) along with a small quantity (<1%) of naturally occurring emulsifiers, such as glycerides, lipids and fatty acids to serve as processing aids. For each of the starches, a series of blends were prepared by varying the relative proportions of the starch and the EVOH in the dry feed. Glycerin (approximately 15% by weight of the dry feed) and some additional water were added to the extruder through liquid ports. The total amount of plasticizer (glycerin and water) inside the extruder varied from 23% to 35%, with average values of 25%, 30%, and 33% for the blends containing waxy maize, native corn, and high-amylose starch respectively. The total output flow rate (from a mass balance of the system) was calculated to be approximately 11-14 kg/h for the neat starches, and 20 kg/h for the blends. The extruder speed during the blending was between 110 and 160 rpm for all the blends, and the maximum temperature was about 190 °C (except for the neat native corn and high-amylose starch, where the temperature had to be lowered). Table 2.1 lists the main series of blends used in this study, their processing parameters, and feed and output rates. As can be seen there, these blends consisted of 30%, 50%, and 70% starch and the rest EVOH (on a dry basis). A second series of blends prepared subsequently (with 15%, 40%, 60%, and 85% starch) was also utilized for the mechanical testing. The composition and processing details for this series are presented in Table A1.1 in Appendix 1.
Table 2.1: Compositions and processing parameters for the main series of starch/EVOH blends (from George et al. 1994).

<table>
<thead>
<tr>
<th>Nomenclature</th>
<th>Starch (wt %)</th>
<th>Feed weight fraction (solids)</th>
<th>Feed weight fraction (glycerin)</th>
<th>Feed weight fraction (water)</th>
<th>Extruder RPM</th>
<th>Extruder peak temperature (°C)</th>
<th>Output flow rate (kg/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Waxy Maize</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>WM 100</td>
<td>100</td>
<td>0.750</td>
<td>0.150</td>
<td>0.100</td>
<td>131</td>
<td>190</td>
<td>11.4</td>
</tr>
<tr>
<td>WM 70</td>
<td>70</td>
<td>0.773</td>
<td>0.150</td>
<td>0.076</td>
<td>114</td>
<td>190</td>
<td>17.3</td>
</tr>
<tr>
<td>WM 50</td>
<td>50</td>
<td>0.732</td>
<td>0.138</td>
<td>0.130</td>
<td>115</td>
<td>190</td>
<td>19.2</td>
</tr>
<tr>
<td>WM 30</td>
<td>30</td>
<td>0.727</td>
<td>0.135</td>
<td>0.138</td>
<td>129</td>
<td>190</td>
<td>17.7</td>
</tr>
<tr>
<td><strong>Native Corn</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NC 100</td>
<td>100</td>
<td>0.671</td>
<td>0.134</td>
<td>0.195</td>
<td>160</td>
<td>119</td>
<td>14.2</td>
</tr>
<tr>
<td>NC 70</td>
<td>70</td>
<td>0.698</td>
<td>0.136</td>
<td>0.166</td>
<td>120</td>
<td>194</td>
<td>19.8</td>
</tr>
<tr>
<td>NC 50</td>
<td>50</td>
<td>0.706</td>
<td>0.133</td>
<td>0.161</td>
<td>125</td>
<td>190</td>
<td>19.2</td>
</tr>
<tr>
<td>NC 30</td>
<td>30</td>
<td>0.735</td>
<td>0.136</td>
<td>0.129</td>
<td>137</td>
<td>190</td>
<td>18.3</td>
</tr>
<tr>
<td><strong>Hylon VII</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HY 100</td>
<td>100</td>
<td>0.686</td>
<td>0.137</td>
<td>0.177</td>
<td>150</td>
<td>170</td>
<td>13.4</td>
</tr>
<tr>
<td>HY 70</td>
<td>70</td>
<td>0.659</td>
<td>0.129</td>
<td>0.212</td>
<td>130</td>
<td>190</td>
<td>18.0</td>
</tr>
<tr>
<td>HY 50</td>
<td>50</td>
<td>0.651</td>
<td>0.126</td>
<td>0.224</td>
<td>149</td>
<td>190</td>
<td>19.8</td>
</tr>
<tr>
<td>HY 30</td>
<td>30</td>
<td>0.702</td>
<td>0.129</td>
<td>0.169</td>
<td>125</td>
<td>190</td>
<td>18.7</td>
</tr>
</tbody>
</table>
2.2.2 Irradiation of Blends

The electron-beam irradiation treatment of the blends was carried out at the MIT High Voltage Research Facility, utilizing a compressed-gas-insulated Van de Graaff Electron Accelerator, with an electron-beam energy of about 2.5 million electron-volts (MeV), and a dose rate of about 2500 Grays sec\(^{-1}\). (1 Gray is the dose corresponding to 1 Joule of energy absorbed per kilogram of irradiated material; 1 Gy = 100 rads) The samples were placed in sealed polyethylene bags prior to the irradiation (this step is carried out on the lab bench, and therefore the pellets are in an air environment) and placed on a moving belt under the beam exit. Since the depth of penetration of the electrons is limited to a few millimeters, care was taken to maintain the sample thickness below approximately 5 mm. The total dose delivered was determined by the belt speed, and the number of passes under the beam exit. The blend pellets were irradiated, as were the samples of filaments prepared from control pellets, at room temperature. The overall dose delivered was in the range of 10 to 200 kGys. (It should be mentioned here that 200 kGys would generally be regarded as a "high" dose for organic polymers.)

The equilibrium water content of the blends depends upon the ambient conditions due to the hydrophilic nature of starch. Since water molecules can have a significant interaction with the radiation, variations in the blend moisture content could lead to variation in the effect the irradiation would have on the blends. The water content can also influence the properties of starches (and hence the blends). For this reason, all the materials were conditioned under fixed conditions for at least one week to regulate the moisture content before each of the experimental steps. This was achieved by placing them in a closed chamber at room temperature (23 °C) and 65% relative humidity. Therefore, the blends were conditioned before and after the irradiation treatment, as well as after the preparation of samples from irradiated pellets.
Table 2.2: Water and glycerin contents of the main series of starch/EVOH blends as compounded, and as conditioned (from George et al. 1994, and Villar et al. 1994).

<table>
<thead>
<tr>
<th>Blend</th>
<th>Glycerin content (as compounded)</th>
<th>Water content (as compounded)</th>
<th>Water content (as conditioned)</th>
</tr>
</thead>
<tbody>
<tr>
<td>WM 100</td>
<td>16.1</td>
<td>7.8</td>
<td>9.5</td>
</tr>
<tr>
<td>WM 70</td>
<td>16.3</td>
<td>5.3</td>
<td>8.3</td>
</tr>
<tr>
<td>WM 50</td>
<td>14.8</td>
<td>9.0</td>
<td>7.1</td>
</tr>
<tr>
<td>WM 30</td>
<td>12.7</td>
<td>7.5</td>
<td>6.0</td>
</tr>
<tr>
<td>NC 100</td>
<td>12.2</td>
<td>15.8</td>
<td>9.8</td>
</tr>
<tr>
<td>NC 70</td>
<td>18.1</td>
<td>12.7</td>
<td>8.5</td>
</tr>
<tr>
<td>NC 50</td>
<td>16.1</td>
<td>9.9</td>
<td>6.9</td>
</tr>
<tr>
<td>NC 30</td>
<td>13.6</td>
<td>6.8</td>
<td>5.9</td>
</tr>
<tr>
<td>HY 100</td>
<td>15.1</td>
<td>8.7</td>
<td>8.1</td>
</tr>
<tr>
<td>HY 70</td>
<td>14.8</td>
<td>10.6</td>
<td>7.9</td>
</tr>
<tr>
<td>HY 50</td>
<td>15.6</td>
<td>12.1</td>
<td>7.5</td>
</tr>
<tr>
<td>HY 30</td>
<td>14.1</td>
<td>8.0</td>
<td>5.9</td>
</tr>
<tr>
<td>EVOH</td>
<td>14.1</td>
<td>0.3</td>
<td>6.9</td>
</tr>
</tbody>
</table>

2.2.3 Chromatography of Irradiated Starches

The experiments were carried out on the DAWN-F (Wyatt Technologies) multiangle laser light scattering (MALLS) detector ($\lambda = 6328$ Å) coupled to a 150-C Gel Permeation Chromatography system (Waters Corp.) using Toyo Soda 4000PWXL and 6000PWXL columns connected sequentially with a guard column, with the temperature of the column compartment at 28 °C. The mobile phase was aqueous 0.5N NaOH with a
flow rate of 0.46 ml/min. The samples for the chromatography were prepared by dissolving them under nitrogen in degassed 0.5N NaOH and subsequently filtering with a Millipore LCR 0.5 μm filter prior to injection. The experiments were performed on the control and irradiated WM 100, NC 100, and HY 100 samples. Dextran standards (Fluka Chemical Co.) were used for calibrating the differential refractometric detector (DRI) detector response. For the experimental samples, the concentration of starch in an elution slice was then obtained from its DRI response. The values of the differential refractive index increment (dn/dc) used in the calculations were as follows: 0.146 for the starches, and 0.142 for dextran (Yu and Rollings 1987). The GPC-LS calculation were performed using the Astra 2.11B software (Wyatt Technology). The inter-detector lag for this experiment was estimated to be 0.28 mls and was obtained by matching the DRI and 90° light scattering signals from an injection of bovine serum albumin (BSA), a monodisperse protein. This value is higher than the value of the inter-detector lag calculated earlier in this lab for the same instrument (see Appendix 2). Analysis of data collected earlier with the same instrument indicate that when that data was collected, the value of the detector lag could not have been as high as the one estimated currently. Therefore, the system must have physically changed over time to account for this increase in the detector lag. It is quite likely that this is due to the effect of the corrosive (0.5 N NaOH) mobile phase on the internal tubing of the GPC system.

2.2.4 Rheological Measurements

The rheological measurements on the blends were obtained using a capillary viscometer (Instron Model 3210 Rheometer coupled with a Model 4505 series Universal Testing Instrument) which basically consists of a barrel that can be heated, and therefore can be used to melt the samples in situ. The action of a plunger is then used to push out the
material through a capillary under controlled conditions of temperature and shear rate. In our experiments, after the capillary had been fixed in the lower end of the barrel and the assembly allowed to reach the set temperature, the material was poured in using a funnel and packed down with the plunger until the extrudate appeared at the lower end of the capillary. The temperature of the barrel and the capillary were controlled by a heating assembly. It was found that the experimental procedure yielded more consistent results if the plunger maintained pressure on the pellets in the time it took for them (5-10 minutes) to reach thermal equilibrium, conceivably due to better compaction. Once the material had melted, the barrel assembly was moved upwards at a fixed velocity and the force exerted by the plunger pushed out the material through the capillary. The shear stress (for a series of different barrel velocities) was obtained from the force required to overcome the pressure drop across the capillary and maintain a steady flow of material. The Rabinowitsch correction factor was calculated to account for the non-Newtonian behavior of the molten blends. The true shear rate at the capillary wall was obtained from the product of this correction factor and the apparent shear rate. The ratio of the wall shear stress and shear rate yielded the melt viscosity at that shear rate. The experimental measurements were carried out at a barrel temperature of 150 °C. This was above the melting point of the plasticized blends, and below the degradation temperatures for the starches. A stainless steel capillary (internal diameter, D, 0.762 mm. and length, L, 50.8 mm; therefore, L/D = 66.7) was used in this study. Bagley correction results from capillaries with lower and higher L/D ratios indicated that the end-effects were negligible for the testing of these blends for our capillary. Overall, shear rates of approximately 1 to 1000 s\(^{-1}\) were achievable in the experiments.
2.2.5 Thermal Analysis

The calorimetric studies were carried out only on 50/50 blends irradiated at 200 kGys, but in this case, the irradiated pellets, the filaments obtained from these pellets, and the respective controls were studied. A differential scanning calorimeter (Perkin Elmer DSC 7) was utilized for this study. The samples were placed in pressure-tight stainless steel pans (which were preferable for these blends due to the presence of a large amount of volatiles), and were heated at a rate of 10 °C/min from 25 to 190 °C. At the end of the run, the sample was cooled at a rate of 10 °C/min until the temperature of the sample was brought down to 25 °C, at which point the second heat was initiated (with the same parameters as the first heat).

2.2.6 Mechanical Testing

For the tensile testing, filaments were prepared using the capillary rheometer from the control pellets as well as the irradiated pellets. For all the samples, the processing through the rheometer was carried out at the same conditions viz., at a temperature of 150 °C, and a plunger velocity of 5 mm/min (corresponding to a nominal shear rate of 133 s⁻¹, and a corrected shear rate of 150-200 s⁻¹, depending upon the sample). The mechanical testing on the conditioned filaments was carried out on an Instron Model 4505 Universal Testing Machine.

Although pneumatic grips were used to hold the filaments during the tensile testing, smooth or serrated grip surfaces were found to unsuitable. The smooth jaws had trouble providing enough friction to hold the filaments tightly, while serrations on the jaw surfaces tended to serve as areas of stress concentrations leading to failure at the grip. A reasonable solution was to deposit a thin cross-linked rubber coating on the gripping surface of the smooth metal jaws. This coating allowed the samples to be held firmly without causing
local necking. With such grips, since the samples are held over a finite length, the effective gauge length can be higher than the actual separation between them, which can affect the absolute values of the initial tensile modulus (as can the compliance of the rubber coating itself). However, since we were mainly interested in estimating the relative property changes for the irradiation-modified samples in comparison to the controls, these grips still serve our purpose as long as the same ones were used for the experimental and control samples with the assumption that the effective gauge length should not vary significantly with the sample. Also, due to the effective gripping point being slightly inside the grip, the filaments were drawn inside the grip at higher extensions. The strain-to-break values were corrected to account for this slip. For each of the samples, at least ten filament samples were tested. The nominal gauge length was 25.4 mm, and the extension rate was 60.96 mm/min, as per ASTM D 3822-91. The data were collected using the Instron mechanical testing program, and reanalyzed using a graphics package (Grapher) to correct for the initial effects at the beginning of the test. Threes sets of samples were studied: the control filaments, filaments prepared from 200 kGys irradiated blend pellets, and 200 kGys irradiated filaments prepared from the control pellets. These samples were studied for a composition range varying from pure EVOH to 70% starch-30% EVOH for each of the three kinds of starches. The effect of the radiation dose for the WM 50, NC 50, and HY 50 filaments was also briefly studied.

2.2.7 Morphological Studies

For the morphology studies of the blends, we chose to study only the filaments that were prepared from 50/50 blend pellets that had received a radiation dose of 200 kGys, since these showed some of the most significant changes in the mechanical properties. The experimental and control filaments were freeze-fractured under liquid nitrogen, and then
suspended in an amylase-amylglucosidase solution (approximately 10 units α-amylase, 3 units β-amylase, and 25 units amyloglucosidase per ml. of a 200 mmol. sodium acetate buffered solution, pH 5.0) for 2 hrs. at 37 °C. The filaments were then rinsed with water, air-dried overnight, and then examined under an environmental scanning electron microscope (ESEM (ElectroScan)). Irradiation of starch seemed to increase its susceptibility to beam damage under regular SEM conditions, and therefore, the milder examination conditions offered by the ESEM were preferred.

2.3 Results and Discussion

The effects of radiation on a polymer in the solid state are a function of a variety of factors such as the type and dose of radiation, and the physical and chemical characteristics of the particular polymer. Radiation with enough energy to cause ionization (such as fast electrons or gamma-rays) can cause significant changes in polymers at the molecular level through the formation of ions and radicals that are, in turn, responsible for chain scission, crosslinking, and other reactions (Charlesby 1991). The interaction of such radiation with the polymer molecules is determined to large extent by the chemical composition of the polymer and the environment of the molecules. Even for a fixed chemical composition, factors such as the morphology of the solid polymer, and its molecular mobility can play a role in determining the final outcome of the radiation effects. For example, from studies on irradiation of crosslinkable semi-crystalline polymers such as polyethylene, it has been inferred that although radiation effects generally predominate in the amorphous regions of the polymer, they can eventually have an impact on the melting and crystallization behavior of the overall sample. Furthermore, if the irradiation is carried out in air, the oxidative reactions (during and subsequent to the irradiation) between the radiation-generated radicals and the oxygen present in the sample can also be significant.
Most studies on the radiation effects on synthetic polymers have focused on the polyethylene because of both its simple molecular structure and its commercial importance. There has been only limited exploration of the effects of radiation on other polymers in the solid state, and very little on the irradiation on EVOH. The formation and decay of alcohol, alkyl, and polyenyl radicals in EVOH irradiated in air and in vacuo has been studied using electron spin resonance (Hama and Hirade 1991). The alcohol radical decay (in air and in vacuo) followed second-order kinetics, indicating a mutual coupling reaction, while the polyenyl radicals decayed in air according to first-order kinetics, attributable to reaction with oxygen molecules that diffused into the solid polymer. Reactions between alkyl radicals and oxygen were also shown to result in the production of moieties such as carbonyl, although these radicals also seemed to lead to the formation of crosslinks. Overall, this work indicated that the irradiation of EVOH results in the production of crosslinks and other products of radical-based reactions. However, other work on the radiation-induced oxidative degradation of EVOH indicates that peroxy radicals could be responsible for scission at the sec-alcohol sites. Ekman and Nasman (1993) have also indicated that electron-beam irradiation of EVOH does not lead to gel formation in the polymer. Data on oxygen transmission and mechanical properties also seem to indicate the relative insensitivity of EVOH to irradiation, at least in the dose ranges relevant to our experiments. Overall, in a sense, the behavior of irradiated EVOH seems to fall between that of polyethylene (mainly crosslinking) and polyvinyl alcohol (mainly scission). In the case of EVOH, the oxygen effects might be lower than those traditionally seen for polyethylene, since the solubility of oxygen in EVOH is lower than in polyethylene.

For starches, it has been shown that ionizing radiation can result in significant physical modification (Whistler and Ingle 1965), resulting in molecular weight reduction through chain scission (as evinced from intrinsic viscosity measurements) (Pruzinec and

33
Hola 1987), as well as a reduction of the strong inter-molecular forces that are often present in native starches (indicated, for example, by an increase in their dispersibility upon irradiation) (Trzebincki and Ehrenberg 1959). For starches (and other hydrophilic polymers), the amount of water can vary significantly depending upon the ambient conditions. This can be an important variable in a radiation experiment; for example, for solid starches exposed to ionizing irradiation, water can have a "protective effect" (Ehrenberg et al. 1957,) and the radiolysis products of water often participate in reactions with the macromolecules (Colonna et al. 1987). Figure 2.1 is a schematic of the degradation processes operative during the radiolysis of starch (Colonna et al. 1987). The process of irradiation can also result in some chemical changes in the starch polymers with introduction of functional groups such as carbonyl and carboxyl moieties (Hebeish 1992) These changes in starch at the inter- and intra-molecular level are likely to affect its processing as well as the eventual morphology (and the properties) of the its blends with other materials.

2.3.1 Chromatography of Irradiated Starches

Figures 2.2 presents the DRI detector trace versus elution volume for the three different starches (control and irradiated samples). It should be kept in mind here that the magnitude of the DRI signal is proportional to the concentration of the macromolecules in any elution slice. As these data indicate clearly, increasing radiation doses result in an increase in the elution volume of the macromolecules. In a GPC experiment, the hydrodynamic size of a molecule determines its time of elution from the columns. Larger molecules have access to a limited number of pores in the packing and elute early, while smaller molecules can access a much larger number of pores resulting in longer elution times. Therefore, a shift of the curve to higher elution volumes upon irradiation is
Fig. 2.1: Overview of the radiation-induced degradation of starch (from Colonna et al. 1987)
consistent with the model of ionizing-radiation-induced chain scission in the starch macromolecules.

Some subtle differences between the response of the different starches to ionizing radiation can be seen. Fig. 2.2a shows the DRI trace for the control and irradiated waxy maize samples. It is seen that the control sample has a peak with a sharp initial rise at an elution volume of about 13.5 mls. This elution volume represents to the exclusion volume for this column set (theoretically corresponding to poly(ethylene oxide) of molecular weight \( \approx 10^7 \) daltons), indicating that the control WM 100 sample consists of (a sizable fraction of) very large molecules that are excluded from the pores of the column (not surprising, given the size of the amylopectin molecules as discussed in Chapter 1). Upon irradiation, the peak broadens, and shifts to higher elution volumes, but stays unimodal in character. This is consistent with the fact that the waxy maize starch contains only one species of molecules; i.e., amylopectin. Fig 2.2b shows the DRI response of the native corn samples. In this case also, the control sample has a steep rise at the exclusion volume of the column set, although the peak has a slight tail. This is probably due to the amylose fraction present in this variety of starch. Upon irradiation, the large initial peak diminishes in size, with the appearance of a broad peak at higher elution volumes. At higher irradiation doses, the overall curve continued to display a somewhat bimodal character.

The high-amylose starch data is somewhat similar (Fig. 2.2c): the control sample displays a bimodal peak, presumably due to the amylopectin, and the (dominant) amylose component. For the irradiated samples, the amylopectin peak slowly reduces in size, while amylose peak shifts to higher elution volumes, and becomes more prominent with increasing radiation dose. In fact, for the 200 kGys irradiated HY 100, only one peak is observable; it is also noticeable that this peak is not as broad as the 200 kGys irradiated samples from the other two starches.
Figures 2.3 shows the molecular weight vs. elution volume plots for these samples as obtained from the light scattering and the DRI traces. It should be mentioned that the calculations that led to these plots are quite approximate since the same value of the dn/dc is used for the irradiated samples as for the controls. (The actual value of the dn/dc is expected to change somewhat since irradiation of starch in air is known to result in the introduction of a variety of functional groups on the glucosidic repeat units.) In any case, these calculations still serve our purpose since we are interested more in the general changes in the molecular weights of the starches rather than their absolute values. Some interesting general trends can be seen here. The data for the lowest elution volumes for all the control samples indicate that the molecular weight is almost constant; these elution volumes contain to the molecules that were excluded from the columns and therefore do not display any chromatographic separation. Furthermore, data for waxy maize and native corn also indicate that the molecular weight vs. elution volume plot is relatively flat. This is somewhat surprising since such a behavior is indicative of molecules that have a range of hydrodynamic sizes for similar molecular weight. Studies with highly branched molecules such as star molecules have indicated that (for a given branch length) the hydrodynamic volume does not change much with molecular weight (Bauer et al. 1989, Roovers et al. 1993). The kind of behavior seen in our case would happen only if these samples have a mixture of molecular species of almost unchanging molecular weights where molecules with a lower degree of branching have longer branches (thus allowing the hydrodynamic volume to change while the molecular weight does not change much). Although theoretically this is possible, it does not seem very likely that this is the case. It seems more likely that the separation mechanism operating on these starch molecules may different from the one assumed for a GPC experiment, and thus the separation may not be based exclusively on hydrodynamic size (which may not be surprising, again given the
large sizes of these molecules). In any case, we see that for all the starches, irradiation leads to the appearance of a molecular weight vs. elution plots that resemble traditional chromatographic data where there is marked drop in molecular weights with increasing elution volumes. It can also be seen that for any given elution volume, starches exposed to a higher radiation doses generally have lower molecular weights. Since molecules with less dense branching possess a lower molecular weight for a fixed hydrodynamic volume, it seems that the starches with higher radiation doses are less branched than the control or lightly irradiated starches. Furthermore, for all the three starches irradiated 200 kGys, the plots are quite similar, i.e., the radiation-based fragmentation renders the samples' chromatographic behavior similar, regardless of their initial differences.

2.3.2 Rheological Behavior

In our data on the rheology of irradiated EVOH pellets, it is seen that there is almost no change in the behavior of the EVOH at the lower radiation doses. The overall shape of the viscosity (η) vs. shear rate (\(\dot{\gamma}\)) curve stays almost unchanged (Figure 2.4a), except that at the higher shear rates, the viscosity seems to drop slightly. This indicates some reduction in the chains (or branches) that are small enough to respond to these higher shear rates (or smaller time scales). At the high radiation dose (200 kGys), the rheology of the EVOH still does not change drastically in comparison to the 20 and 80 kGys cases, except an increase in the viscosity in the low shear rate regime is also seen. It is possible that this behavior for the 200 kGys case could be a result of some radiation-induced cross-linking, though not enough to cause gelation.

The starches, on the other hand, show a notable downwards shift in the viscosity for all shear rates due to molecular scission (Figures 2.4b - d), with the overall amount of the shift increasing monotonically with increased radiation doses. There are, however,
some difference among the starch samples. For the waxy maize control sample (Fig. 2.4b), a discontinuity was observed in the η vs. γ plot at a shear rate of about 60 s⁻¹ that is presumably due to melt fracture. With a radiation dose of 20 kGy, this was eliminated, and a substantial reduction in the viscosity was seen at lower shear rates. At 80 kGy, a further reduction in the viscosity was seen through the whole range of shear rates over which the measurements were made. The dose of 200 kGy had a drastic effect upon the pellets, causing them to foam and swell up. The viscosity of the resulting material was too low to measure in our capillary rheometer setup. For the high-amylose starch (Fig. 2.4c), the viscosity was less affected by the irradiation treatment, with the 20 kGy sample showing almost no changes, and with the viscosity eventually dropping across the whole range of shear rates with higher radiation doses. For the native corn starch (Fig. 2.4d), the behavior was a little bit more complex. The control sample showed a distinct difference in the shear-thinning behavior above and below approximately 100 s⁻¹. At the lower shear rates, the trend was closer to that of the high-amylose starch, and at the lower shear rates, more like that of the waxy maize sample. This seems to indicate that at lower shear rates, the linear amylose molecules dominate the viscosity of the sample, while at the higher shear-rates, the contribution of the amylopectin molecules start playing a role in determining the overall viscosity of the sample. For the irradiated samples, a reduction in the viscosity was observed, and with increasing irradiation, the shear-thinning behavior seemed to become more uniform across the range of shear rates. Above and beyond these finer details for the individual starches, these data show that as a general trend, starches with higher amylopectin content displayed relatively greater changes in their rheological behavior, for a given radiation dose. However, the GPC data indicate that the HY 100 samples suffers at least much molecular scission as the WM 100 and the NC 100 samples. Such a difference between the melt and solution behavior of the irradiated and control
samples might be explained by the behavior of the amylose present in these starches. Amylose molecules are known to form helical complexes with internal lipids present in maize starches in their native state (Galliard and Bowler 1987); the HY 100 displays the formation of such complex to a much greater extent than the NC 100 (Simmons 1994). Such a conformation of the amylose molecules could be responsible for the extremely high viscosity (and shear rate dependence) displayed by the HY 100 control as compared to the WM 100 or NC 100. Although irradiation of the high-amylose starch might cause scission, the fragmented amylose macromolecules might well retain such a structure, allowing the irradiated HY 100 to display a melt viscosity higher the irradiated WM 100 or NC 100.

The rheological behavior of the control blends of starch with poly(ethylene-co-vinyl alcohol) has been shown to vary with the relative fractions of the starch and the EVOH in the blend, as well as with the composition of the starch (Villar et al. 1994). For the irradiated materials, since the EVOH does not seem to be affected much by the radiation, changes in the rheology of the irradiated blends generally follow the changes in the rheology of the starch components. Accordingly, the waxy maize blends show the greatest overall reduction in the viscosities (Figures 2.5a-c) followed by the native corn (Figure 2.6a-c). The high-amylose blends showed the least reduction in viscosity (Figure 2.7a-c); in fact, for some of the irradiated Hylon blends, the viscosity is even higher than the control samples for some shear rates. This could possibly result from some grafting between the starch and EVOH chains, though this could not be proved. In general, though, for the starches we see that the magnitude of the changes increase with increasing amylopectin content, for a given radiation dose.

The shear stress ($\tau$) vs. shear rate data are plotted in Figure 2.8 - 2.10. It is seen here that the shear stress in the EVOH melt is higher than that of the pure waxy maize and
lower than that of the Hylon VII at almost all values of the shear rates. The native corn starch has a shear stress higher than the EVOH for the lower shear rates; above some critical shear rate, the curves cross over with the EVOH displaying the higher shear stress. The data for the series of blends over the range of starch/EVOH compositions display clear differences among the different starch types. The Hylon blends display a consistent trend going from HY 100 to EVOH, with the slope of the $\tau$ vs. $\dot{\gamma}$ curve increasing from a low value for the pure starch to the high value for the EVOH. At the higher shear rates, the shear stresses for the HY 50 and HY 30 blends converge to values similar to those for EVOH, but overall it is seen that the shear stresses for all the Hylon blends are higher than the pure EVOH. These high stresses are presumably due to the presence of the linear amylose molecules. For the waxy maize, the WM 100 and WM 70 are close together (although the WM 70 curve is a little bit lower than the WM 100), while WM 50 and WM 30 are similar to each other, but with shear stresses higher than the former pair across the range of shear rates in our experiment. Unexpectedly, though, the WM 50 and WM 30 display shear stress values higher than that of EVOH at the low shear rates, but tending to the EVOH values at higher shear rates. One potential explanation for this behavior could be that the WM 50 and WM 30 blends tend to act as an EVOH matrix filled with waxy maize granules (or fragmented granules), with the former supporting most of the shear stress. Such an explanation has been proposed for similar behavior in semiconcentrated fiber suspensions (Bibbo et al. 1985). The native corn showed a behavior somewhat in between the other two starches. The NC 100 and NC 70 curves show a trend similar to each other, but the NC 70 has shear stresses much lower than NC 100 for a fixed shear stress. This is reminiscent of the behavior of the waxy maize counterparts of these two blends, except the magnitude of the offsets between the 100% starch and 70% starch containing blends is much higher for the native corn-containing samples. The NC 50 and NC 30 curves are
close to the EVOH curve and as with the other starches, the NC 30 curve converges to that of EVOH at high shear rates. This general trend for the 30% starch blends is not surprising; at higher shear rates (which also correspond to higher shear stresses), the smaller EVOH molecules are the most likely to dominate the response of the blend.

The rheological behavior of polymer blends as a function of their composition and of the viscosities of the individual components is of practical significance since an understanding of such behavior can assist in determining desirable blend compositions and their processing parameters. The log-additivity model is often used as a simple method to assess the behavior of the mixtures of the polymers. For ideal blends, the zero-shear viscosity of the blend should be a weighted log-addition of the zero-shear viscosity of the individual fractions. Positive or negative deviation of the blend from this ideal behavior can gives some insight into the interactions between the components. In the absence of zero-shear data, it has been suggested that the assessment be carried out at constant shear rate or constant shear stress (Utracki 1983, 1991).

Figures 2.11 - 2.13 show the application of the log-additivity rule at constant shear stress. For the waxy maize control blends, WM 30 and WM 50 show a positive deviation from the from the ideal mixing rule denoted by the dotted line. However, for WM 70, at low shear stress, the value of the corrected viscosity is close to what is expected from an ideal mixing, but at higher shear stress, a negative deviation is seen. For the irradiated blends, the viscosity for the WM 100 case is extrapolated from the data for the 20 and 80 kGys irradiated blends (since the rheology for 200 kGys irradiated pellets could not be carried out). It is then seen that these irradiated blends exhibit a positive deviation at all shear stresses and all blend compositions. The native corn control blends show a negative deviation at the lower shear stress, and a positive-negative deviation at the higher shear stress value. These blends irradiated with 200 kGys dose exhibit a positive-negative
deviation at the lower shear stress also. The Hylon VII control blends are different from
the those of the other two searches in that they show a strong negative deviation at across
the range of blend compositions. In fact, the corrected viscosity is almost constant for the
blends containing 50% or less starch. The irradiated blends, on the other hand, show a
smaller negative deviation for the HY 30 blend at lower shear stresses, and a positive
deviation at all considered shear stresses, with the amount of the deviation increasing with
the starch content.

Applying the log-additivity rule at constant shear rates (Figures 2.14 - 2.16), we
see that the waxy maize blends exhibit a behavior similar to that at constant shear stress.
The control WM blends exhibit a positive deviation for almost all the cases, except for the
WM 70 blends where the slight positive deviation at the low shear stress changes to a
negative deviation, increasing with increasing shear rates. The trend does not change much
for the irradiated samples, except that the negative deviation for the WM 70 blends is
eliminated. It is the other two starch blends that show a striking difference from the
constant shear stress plots. At constant shear rates, the native corn blends follow the ideal
rule of mixtures almost across the board for all blend compositions and most shear rates. It
is only at the very high shear rates that a slight positive-negative deviation behavior can be
seen. The behavior of the irradiated NC blends is more curious however. At the lower
shear rates, the NC 30 and NC 70 blends display some positive deviation and the NC 50
shows a negative deviation. Still, overall these blends still do not show much of a
deviation from the rule of mixtures. The Hylon VII blends follow a pattern similar to that
of the native corn; at almost all shear rates, their corrected viscosity is close to that of the
rule of mixtures. The irradiated Hylon VII blends show a slight positive deviation,
especially at the low shear rate, and at higher starch contents. Overall, then, it seems that
the rule of mixtures at constant shear rate seems to predict the viscosity of our blends that contain starch with amylose fractions.

2.3.3 Thermal Behavior

Data from the DSC studies on the control and irradiated EVOH and 50/50 blend pellets are shown in Table 2.3. (Only data for the second heat are tabulated here. Detailed data on control and irradiated pellets and filaments are shown in Appendix 1, Table A1.2.) The DSC scans on the control and irradiated EVOH pellets do not yield any notable change in the shape, size or temperature of the endotherm, indicating that irradiation does not result in significant modification to the EVOH, at least not enough to cause an observable change in the re-crystallization behavior of the irradiated material. This is in contrast to the observations for polyethylene, where both the overall level of crystallinity and the peak melting temperature decrease for irradiated samples. (Giezlenz 1982, Zoepfl 1984) The melting and crystallization temperatures for the EVOH pellets used in this study were lower than those reported for pure EVOH (Blackwell 1986), but that is expected given the high level of the plasticizer content in the materials used here.

The endotherm in the 50/50 blend control pellets (HY 50, NC 50, and WM 50) corresponds to the melting of the EVOH crystallites. There are some differences among the blends in the peak temperature of the endotherm, as well as in the heat of fusion per unit mass of EVOH in the sample. The WM 50 and HY 50 pellets display a endotherm peak at temperatures slightly lower than that of the (glycerin-containing) EVOH, but the NC 50 has a melting point slightly higher than that of the EVOH. The area under the endotherm peak (corresponding to the crystallizable fraction in the EVOH) reduces as the amylose content of the starch used in the blend is increased. This could be attributable to
Table 2.3: DSC data (second heat) for control and 200 kGys irradiated EVOH and 50/50 blend pellets.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_{\text{onset}}$ (°C)</th>
<th>$T_{\text{peak}}$ (°C)</th>
<th>$\Delta H$ (J/g sample)</th>
<th>$\Delta H$ (J/g EVOH)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EVOH (control)</td>
<td>124.0</td>
<td>140.1</td>
<td>39.26</td>
<td>49.73</td>
</tr>
<tr>
<td>EVOH (200 kGys)</td>
<td>122.0</td>
<td>139.6</td>
<td>39.39</td>
<td>49.90</td>
</tr>
<tr>
<td>WM 50 (control)</td>
<td>128.7</td>
<td>137.4</td>
<td>18.06</td>
<td>46.25</td>
</tr>
<tr>
<td>WM 50 (200 kGys)</td>
<td>117.9</td>
<td>129.2</td>
<td>19.41</td>
<td>49.70</td>
</tr>
<tr>
<td>NC 50 (control)</td>
<td>136.0</td>
<td>144.0</td>
<td>17.36</td>
<td>45.09</td>
</tr>
<tr>
<td>NC 50 (200 kGys)</td>
<td>114.4</td>
<td>125.9</td>
<td>16.21</td>
<td>42.10</td>
</tr>
<tr>
<td>HY 50 (control)</td>
<td>123.7</td>
<td>135.8</td>
<td>14.31</td>
<td>37.22</td>
</tr>
<tr>
<td>HY 50 (200 kGys)</td>
<td>106.2</td>
<td>120.3</td>
<td>14.32</td>
<td>37.24</td>
</tr>
</tbody>
</table>

The linear amylose molecules hindering the crystallization of the EVOH. During disruption of the starch granules, amylose molecules leach out before the amyllopectin; therefore, during the extrusion, as the starch granules lose structure, it is possible that the starches containing higher amylose fractions could be responsible for a greater amount of relatively free amylose molecules interacting with the EVOH.
Examination of the irradiated blends indicates some noticeable changes upon irradiation. For all the starches, the irradiated blend pellets yield endotherms at significantly lower temperatures in comparison to their control counterparts, although the area under the peak does not change too much. Since for the EVOH pellets without any starch, no drop in the melting temperature was seen, it is possible that in these blends, the low-molecular weight degradation products of the starches could be acting as additional plasticizers for the EVOH, thus lowering its melting point.

2.3.4 Mechanical Properties

Figure 2.17 shows the changes in the initial tensile modulus, the nominal ultimate tensile stress, and the ultimate tensile strain of starch/EVOH blends upon 200 kGys irradiation, as compared to values for the control blends. Figure 2.18 shows changes in the same parameters (once again relative to the control materials) for 50/50 blends for a dose of 80 and 200 kGys. For these sets of data, the tests on irradiated materials were on filaments prepared from irradiated pellets (referred to as FIP). Figures 2.19 shows the changes in the same three parameters (between irradiated and control samples), except the irradiated samples here are filaments that were irradiated after preparation from unirradiated pellets (referred to as IF). Figure 2.20 shows representative nominal tensile stress versus strain curves for the EVOH and the 50/50 starch blends irradiated 200 kGys. (The detailed values of the properties of these materials are reported in Appendix 1, Table A1.3)

As with the rheological behavior, the mechanical properties of the irradiated EVOH did not show major changes as compared to the control samples (Figs. 2.17, 2.19). The tensile modulus of the FIP, as well as the IF samples drops slightly at low doses (20 kGys), but increases somewhat subsequently with increasing doses. The stress- and strain-to-break values for both the sets of filaments show almost no change for the 20 kGys
dose, but then drop consistently (but only marginally) with increasing radiation dose. This trend correlates well with the rheological behavior of the irradiated EVOH, indicating that at the higher doses, some crosslinking occurs in the EVOH, which could manifest itself in higher values of the tensile modulus, but lower ultimate tensile extension. These observations are consistent with the work of Hama and Hirade (1991), i.e., overall the properties of EVOH are not modified significantly in the range of doses relevant to our experiments, although some crosslinking does occur at the higher doses. Interestingly, even though the trends for the two sets of filaments are similar, the overall magnitudes of the changes are different, with the filaments from irradiated pellets displaying slightly lower modulus, but higher stress-and strain-to break values. Any crosslinking caused in the EVOH is likely to be in amorphous part. Subsequent melting and re-solidification of these pellets (as is the case for the filaments from irradiated pellets) would actually hinder re-crystallization somewhat, therefore leading to smaller crystalline fractions in the material. The tensile modulus is dependent upon the crystalline fractions of a semi-crystalline polymer, while the stress-and strain-to break values depend more upon the amorphous fraction (Harnischfeger et al. 1991). The values of the tensile modulus for our EVOH control samples (and even for the blends) are lower than those reported by George et al. (1994), but as mentioned earlier; this is likely, at least in part, due to our grips. Therefore, the absolute numbers for the tensile modulus of these samples should be regarded only as rough estimates of the real values; still, the discernible trends in the changes of this property (for the irradiated samples as compared to the controls) should still hold.

The mechanical properties of the FIP samples prepared from blends of starch and EVOH, however, show some significant changes as a consequence of irradiation (Fig. 2.17). For the samples containing 70% starch or more, the mechanical properties deteriorated greatly with 200 kGys radiation dose; in fact, it was not possible to obtain
meaningful data from mechanical measurements on these samples. Such a sharp degradation in mechanical properties indicates that for these blends, the starch must be the dominant continuous phase on which the mechanical properties of the blends must be dependent; since starch is the only component of these blends that degrades significantly upon irradiation.

The same was not true of the blends with starch content 50% or less. For these blends, it is noticeable that the trends for the FIP and the IF samples are very different from each other (Figs. 2.17, 2.19). The properties of the blends' IF samples change in a fashion somewhat similar to the EVOH IF samples, i.e., the modulus increases slightly while the stress-and strain-to-break values drop down. However, the 200 kGys FIP samples show a very different behavior compared to the controls. The WM 50 and WM 30 filaments show an increase in the initial modulus, strain- and stress-to-break, with the effects being more pronounced for the WM 50. The NC 50 and NC 30 filaments show a trend similar to the waxy maize filaments, except that the magnitude of the differences between the control filaments and the samples prepared from irradiated pellets are not as high. The HY 50 and HY 30 filaments show small or no differences from the control filaments in the initial modulus and strain-to-break, while the stress-to-break values drop down.

As an aside, it should also be mentioned that the diameters of filaments obtained from the starch/EVOH blends was higher than that of the pure EVOH, though this might partly be due to some drawing of the EVOH filaments under their own weight as they exit the capillary. More interestingly, it was also noticed that the diameter of the filaments produced from irradiated pellets are somewhat greater than those produced from the control pellets (for EVOH content of 50% or more) indicating some general increase in the degree of die swell.
Irradiation studies on immiscible polymer blends have indicated that the individual components show the same response to radiation as the respective homopolymers. However, since the individual components of the blends can display very different responses to radiation, the overall properties of the blends can be significantly modified by radiation (although it is often difficult to predict the overall consequences of the irradiation a priori). Much of the work on radiation modification of polymer blends has dealt with rubber modified thermoplastics, or compatibilized blends (where crosslinking of the rubber phase or formation of crosslinks at the interface is mainly responsible for changes in the properties of the blends). These systems are very different from ours, and therefore it is difficult to relate our observations to the understanding gained from these other studies.

There have been a few experimental studies of the effect of ionizing radiation on the properties of polypropylene-containing blends (Thomas et al. 1987, Minkova and Nikolova 1987). Upon irradiation, polypropylene was indicated to display chain scission predominantly (Thomas et al. 1987, Minkova and Nikolova 1987) or a balance of crosslinking and chain scission (Harnischfeger et al. 1991). The second component of the blend in these studies underwent crosslinking upon irradiation. Furthermore, in all of these studies, irradiation was carried out on prepared samples with no further processing steps subsequent to the irradiation, i.e., the morphology remained fixed (similar to our irradiated filament samples). It was observed that generally with increasing radiation doses, while the tensile elastic modulus increased, the tensile strength dropped somewhat and and elongation at break dropped quite significantly. Thomas et al. noted that for their blends containing 70% poly(ethylene-vinyl acetate), the mechanical properties showed a remarkable difference in that the elongation at break and increased dramatically upon irradiation. This was attributed to the continuous interpenetrating structure formed by this blend where, under the action of radiation, the crosslinking of the rubbery phase and the
scission in the plastic phase led to a greater extensibility of the blend for reasons not completely explained by the authors. However, most of the general observation of these two studies are consistent with the model of a blend in which one phase displays crosslinking and the other chain scission upon irradiation (if the morphology remains fixed between the irradiation and testing steps). These results are similar to our IF samples. However, such a model cannot be simply applied to our FIP samples since the melt-processing subsequent to irradiation allows for changes in morphology as discussed in the next section. Huang (1993) indicated that gamma-irradiation of samples prepared from starch/EVOH blends can influence their mechanical properties, but once again this experiment is similar to our studies on IF samples since no melt-processing was carried out subsequent to the radiation treatment.

2.3.5 Morphology

The morphological studies on the filaments obtained from the 200 kGys irradiated 50/50 blend pellets, and the respective control filaments indicate some interesting changes upon irradiation. In the ESEM micrographs shown in Figure 2.21 - 2.26, there are two kinds of pictures: surfaces of the filaments, and the enzymatically etched cross-sections of the filaments. For the latter kinds of micrographs, dark cavities represent the areas that initially contained starch (which was subsequenty removed by the enzymatic etching).

The WM 50 samples showed the most striking changes. The surfaces of the control filaments have a slightly rough appearance, while the 200 kGys FIP surfaces are distinctly smoother (Fig. 2.21). The cross-sections of the filaments prepared from the control pellets also show discrete (almost round or oblate) starch domains with a distribution of sizes (in the approximate range of 1 to 3 microns) dispersed in a matrix of the synthetic polymer (Fig. 2.22). It can also seen that often thin webs of EVOH separate
the starch domains. The structure of the filaments prepared from the irradiated pellets is distinctly different (Fig. 2.22b, c), whereby the starch domains are generally much larger in size (roughly 3-10 microns across), and penetrate deeper below the fracture surface. In fact, the two components almost seem to be forming a co-continuous interpenetrating morphology (much more obvious in the higher magnification micrograph).

The surface of the NC 50 filaments (Fig. 2.23) also show a difference between the control and the 200 kGys FIP sample (though not as much as the WM 50 case). The cross-sections of the control and the FIP sample (Fig. 2.24) also show similarities to their WM 50 counterparts, though once again it can be seen that the irradiated native corn sample does not show as striking a change in the structure as the irradiated waxy maize sample. It should be mentioned here that for both the WM and NC cases, the morphology was not always uniform across the cross-section of the filaments; the micrographs shown are generally representative of the structures, however.

For the HY 50 samples, the surfaces of the two filaments did not show much of a difference (Fig. 2.25). The etching the cross-sections of these filaments did not seem to be very successful for reasons not completely understood; as can be seen, there are no clear domains of (etched out) starch (Fig. 2.26). Given the sizes of the starch molecules, it is difficult to imagine that phase separation does not occur between the starch and the EVOH. It is possible that the interactions between the linear amylose molecules and the EVOH prevent the formation of clear domains which can be attacked by the enzyme. There are some differences between the micrographs for the control and the 200 kGys FIP sample, but to any conclusions from these would be meaningless.

Obviously, the change in the structure of the NC and WM blends came about during the melt-reprocessing of the irradiated pellets through the capillary set-up used to produce the filaments. As mentioned earlier, in our blends, the radiation has the effect of
modifying starch to a much greater extent than the synthetic polymer. Therefore, the differences observed between the control and irradiated blends can be mostly attributed to the differences in the starch present in the two blends. It can be imagined that the molecular scission in the starch macromolecules increases their mobility in the blend, especially given the fact that the waxy maize and native corn starch used in the blending must have contained strong inter-molecular forces (since complete dissolution of the precursor or extruded waxy maize and native corn starches was not possible even in good solvents such as alkali). It is also possible that some interfacial reactions might have occurred between the starch and EVOH phases during irradiation, but at present there is no support for this hypothesis.

Other studies in literature on blends of starch and synthetic polymers indicate that unmodified starch blended with thermoplastics maintains its granular shape despite the action of the shear forces during the processing (Griffin 1974, Maddever and Chapman 1989, Evangelista et al. 1991, Penansky et al. 1991, Ramsay et al. 1993). This starch filler does not serve any reinforcing function, which is not surprising since there is no mechanism of stress transfer across the interface between the starch and the thermoplastic matrix. In such cases, the discrete starch granules or domains would tend to act almost as voids for the tensile stress fields. Consequently, in almost all cases, a decrease in the elongation to break and the ultimate tensile strength is seen as increasing amounts of starch are blended into a thermoplastic. Processing methods that allow an increased dispersion of starch generally have resulted in products with better properties. The dispersion of starch can be attained by gelatinization of the starch previous to the mixing (Oley et al. 1980) or through chemical modification such as derivatization of the starch hydroxyl groups to acetate or hydroxypropyl moieties (Swanson 1988). Surface modification of starch granules to increase their hydrophobicity also results in marginal improvements in
properties of starch blends with polyethylene (Evangelista et al. 1991). It has also been shown that co-precipitation of starch xanthide and thermoplastics from solution (Westhoff et al. 1974) or casting of such blends from aqueous dispersions (Otey et al. 1977) leads to films with better mechanical properties than those made from dry-milled blends. The improved mixing between the blend components was proposed as being responsible for this difference. Otey et al. (1987) also showed that the dispersion of the starch can be made more effective not only through the traditional gelatinization using a combination of heat and moisture, but also through the use of urea and other polyols that allow the preparation of well-mixed blends through semi-dry processing.

All this indicates that the dispersion of starch in its blends with other thermoplastics plays a crucial role in the eventual properties attainable by the blend. If the starch is blended with a thermoplastic such that it does not lose its granular structure, then the blend is likely to behave like a thermoplastic with non-reinforcing filler. If the starch granular structure is disrupted completely before or during blending, then the starch is likely to act more like a traditional polymer in that it is mobile at a molecular level during blending. It is also mentioned (Otey et al. 1987) that interactions between starch and thermoplastic may prevent retrogradation of the starch, and therefore allow the blend to retain desirable mechanical properties even upon aging. In our case, the irradiation of the granular native corn and waxy maize starches in their blends with EVOH should certainly allow for much better mobility of the starch, and hence lead to a different microstructure for the blend.

The behavior of the high-amylose starch-containing blends, though very different from the native corn and waxy maize-containing blends, seems consistent across the various probes of structure and properties employed in this study. The rheological, DSC, mechanical property measurements, and the morphology studies all seem to indicate that there might be some interactions between these high-amylose starch molecules and the
EVOH. Such an interaction might underlie the increase in the viscosity of the irradiated HY blends, the lower levels of crystallinity obtained in the DSC, and the comparative insensitivity of the mechanical properties and the structure these blends to radiation. It should also be kept in mind that the precursor Hylon material was an acid-modified variety, and hence certainly lacked the strong inter-molecular forces most likely present in the (unirradiated) granular waxy maize and native corn starches used in this study.

2.4 Conclusions

Irradiation of starch by an (ionizing) electron-beam results in significant physical modifications at the molecular level, of which the primary ones are the scission of bonds and disruption of inter-molecular structures. This is evident from the gel permeation chromatography carried out on the irradiated starches, as well as from the rheological behavior of the irradiated starches and irradiated-starch-containing blends. In contrast, the synthetic polymer that forms the second component of the blends used in this study seems to be relatively unaffected by irradiation. The filaments prepared from irradiated blend pellets show a marked change in their microstructure and an improvement in mechanical properties (such as stress- and strain-to-break) as compared to the filaments prepared from control pellets (for starch content less than 50%); irradiation of the latter filaments does not result in an improvement of their properties. Presumably the melt processing of the irradiated pellets allows the formation of the modified microstructures observed in the micrographic examination of the cross-sections of the filaments, especially those containing waxy maize starch. This can be attributed to the greater mobility of the (fragmented) irradiated starch present in the blend.

Disruption of granular structure and/or macromolecular scission can also be effected by other treatments such as acid degradation or mechanical processing, but these
are generally complex and time-consuming in comparison to irradiation which does not require much preparation of the raw materials, is quick, and requires no subsequent purification. Consequently, irradiation-based *physical* modification of starch seems to offer a simple and straightforward method (that could be industrially viable) to effect desirable improvements in the properties of blends of starches with thermoplastic materials.
Fig. 2.2: DRI detector traces from chromatography of control and irradiated starches: (a) WM 100
Fig. 2.2: (b) NC 100
Fig. 2.2: (c) HY 100
Fig. 2.3: Molecular weight as a function of elution volume for control and irradiated starches: (a) WM 100
Fig. 2.3: (b) NC 100
Fig. 2.3: (c) HY 100
Fig. 2.4: Melt viscosity as function of shear rate for neat starches and EVOH (all containing glycerin and water as noted in Table 2.2): (a) EVOH
Fig. 2.4: (b) WM 100
Fig. 2.4: (c) HY 100
Fig. 2.4: (d) NC 100
Fig. 2.5: Melt viscosity as function of shear rate for waxy maize/EVOH blends.
(a) WM 70
Fig. 2.5: (b) WM 50
Fig. 2.5: (c) WM 30
Fig. 2.6: Melt viscosity as a function of shear rate for native corn/EVOH blends: (a) NC 70
Fig. 2.6: (b) NC 50
Fig. 2.6: (c) NC 30
Fig. 2.7: Melt viscosity as a function of shear rate for Hylon VII/EVOH blends: (a) HY 70
Fig. 2.7: (b) HY 50
Fig. 2.7: (c) HY 30
Fig. 2.8: Shear stress as a function of shear rate for Hylon VII/EVOH blends: (a) Control
Fig. 2.8: (b) Irradiated 200 kGys
Fig. 2.9: Shear stress as a function of shear rate for waxy maize/EVOH blends: (a) Control
Fig. 2.9: (b) Irradiated 200 kGys
Fig. 2.10: Shear stress as a function of shear rate for native corn/EVOH blends:
(a) Control
Fig. 2.10: (b) Irradiated 200 kGys
Fig. 2.11: Melt viscosity of waxy maize/EVOH blends as a function of starch fraction (for fixed shear stress values): (a) Control, (b) Irradiated 200 kGys. Dashed line represents ideal mixing rule.
Fig. 2.12: Melt viscosity of native corn/EVOH blends as a function of starch fraction (for fixed shear stress values): (a) Control, (b) Irradiated 200 kGys. Dashed line represents ideal mixing rule.
Fig. 2.11: Melt viscosity of Hylon VII/EVOH blends as a function of starch fraction (for fixed shear stress values): (a) Control, (b) Irradiated 200 kGys. Dashed line represents ideal mixing rule.
Fig. 2.14: Melt viscosity of waxy maize/EVOH blends as a function of starch fraction (for fixed shear rate values): (a) Control, (b) Irradiated 200 kGys. Dashed line represents ideal mixing rule.
Fig. 2.15: Melt viscosity of native corn/EVOH blends as a function of starch fraction (for fixed shear rate values): (a) Control, (b) Irradiated 200 kGys. Dashed line represents ideal mixing rule.
Fig. 2.16: Melt viscosity of Hylon VII/EVOH blends as a function of starch fraction (for fixed shear stress values): (a) Control, (b) Irradiated 200 kGys. Dashed line represents ideal mixing rule.
Fig. 2.17: Changes in mechanical properties (relative to controls) of blends upon irradiation (200 kGys), as a function of starch fraction (Test samples: filaments from irradiated pellets (FIP), control samples: filaments from unirradiated pellets): (a) Elastic tensile modulus
Fig. 2.17: (b) Nominal ultimate tensile strength
Fig. 2.17: (c) Ultimate tensile strain
Fig. 2.18: Changes in mechanical properties (relative to controls) of 50/50 blends upon irradiation, as a function of radiation dose (Test samples: filaments from irradiated pellets (FIP), control samples: filaments from unirradiated pellets): (a) Elastic tensile modulus
Fig. 2.18: (b) Nominal ultimate tensile stress
Fig. 2.18: (c) Ultimate tensile strain
Fig. 2.19: Changes in mechanical properties (relative to controls) of 50/50 blends upon irradiation, as a function of radiation dose (Test samples: irradiated filaments (IF), control samples: filaments from unirradiated pellets):
(a) Elastic tensile modulus
Fig. 2.19: (b) Nominal ultimate tensile stress
Fig. 2.19: (c) Ultimate tensile strain
Fig. 2.20: Representative nominal stress vs. strain curves for control filaments, filaments from 200 kGys irradiated pellets (FIP), and 200 kGys irradiated filaments (IF): (a) EVOH, (b) HY 50
Fig. 2.20: (c) NC 50

Fig. 2.20: (d) WM 50
Fig. 2.21: Micrographs of WM 50 filament surfaces: (a) Control filament, (b) Filament from 200 kGys irradiated pellets (FIP)
Fig. 2.22: Micrographs of cross-sections of WM 50 filaments, subsequent to enzymatic treatment to remove starch. The dark areas correspond to the regions where starch was etched out. (a) Control filament (1000x), (b) Filament from 200 kGys irradiated pellets (FIP) (1000x)
Fig. 2.22: (c) Filament from 200 kGys irradiated pellets (FIP) (2000x)
Fig. 2.23: Micrographs of NC 50 filament surfaces: (a) Control filament, (b) Filament from 200 kGyrs irradiated pellets (FIP)
Fig. 2.24: Micrographs of cross sections of NC 50 filaments, subsequent to enzymatic treatment to remove starch. The dark areas correspond to the regions where starch was etched out. (a) Control filament (1000x), (b) Filament from 200 kGys irradiated pellets (FIP) (1000x)
Fig. 2.25: Micrographs of HY 50 filament surfaces: (a) Control filament, (b) Filament from 200 kGys irradiated pellets (FIP)
Fig. 2.26: Micrographs of cross-sections of HY 50 filaments, subsequent to enzymatic treatment to remove starch. The dark areas correspond to the regions where starch was etched out. (a) Control filament (1000x), (b) Filament from 200 kGys irradiated pellets (FIP) (1000x)
3.1 Introduction

Starch or its components have been generally been found to be unsuitable for use by themselves in applications requiring reasonable mechanical integrity. For example, even though films of pure amylose (prepared by a solvent-casting procedure) were found to be self-supporting and to possess a high tensile modulus, they were only somewhat flexible and displayed a very low ultimate tensile extension (Wolff et al. 1951a). In addition, due to the hydrophilic nature of amylose, the wet strength of these films was also found to be quite low. Addition of amyllopectin was found adversely affect the flexibility, tensile strength, and elongation to break.

Since the derivatization of the glucosidic hydroxyl groups can be carried out with relative ease, various kinds of chemical modifications of starches have been attempted along this route in order to modify their chemical and physical properties. Changes in these properties are highly dependent upon the nature of the chemical group that is appended to the hydroxyl groups, and the extent of the derivatization. This has found diverse applications such as the modification of the gelatinization behavior of granular starches, control of the gelling and retrogradation of amylose-containing starches, and increasing the hydrophilicity of starches as well as imparting hydrophobic or ionic character through incorporation of suitable moieties (Rutenberg and Solarek 1984). The modification of the interaction of starch-solvent interactions, and concomitantly, the solution properties of starch (or its components) is relatively easily achievable with the addition of a small number of chemical groups. In fact, for many industrial applications, only a low level of chemical modification is generally needed to suitable alter the properties
of starch; most commercially used starches generally have a degree of substitution less than 0.2 (Rutenberg and Solarek 1984). (In starch chemistry, the extent of conversion is generally represented by the degree of substitution (D.S.) which is defined as the moles of substituents per D-glucopyranosyl structural unit of the starch polymer; with three hydroxyl groups per unit, the theoretical maximum D.S. is 3). High levels of substitution, on the other hand, can completely transform the character of starch. This is true not only of starch but of most polysaccharides; for example, a variety of highly substituted cellulose esters have been used for various applications since the last century (Barsha 1954, Malm and Hiatt 1954).

A number of reports exist in literature pertaining to the preparation of esters of starch or its components with high degrees of substitution with the ultimate aim of significantly modifying the physical-chemical properties of starches, and imparting suitable mechanical characteristics such as so render them more useful as engineering materials than the pure precursors. Reactions on starches to prepare highly substituted derivatives are not easy, mainly because of the almost impossible proposition of dissolving granular starch in a suitable medium without significant degradation. Among the various methods of ester preparation that have been attempted to overcome this hurdle are the gelatinization pre-treatment of starch (Mullen and Pacsu 1942), dispersion in inert solvents at elevated temperatures (Carson and Maclay 1946, Gros and Feuge 1962) and at room temperatures (Potter and Hassid 1948). The addition of the ester group is carried out by employing the appropriate acid anhydride or the acid chloride (with the latter generally being more effective for the higher esters) in the presence of pyridine which serves the dual purpose of catalyst as well as solvent.

Mullen and Pacsu (1943) briefly evaluated the properties and potential industrial applicability of some corn starch esters. They found that although starch esters such as the
butyrate and caproate can be molded, their general mechanical properties were not very satisfactory. Addition of plasticizer was found to remedy the situation somewhat. Wolff et al. (1951b, c) prepared triesters of amylose, amylopectin, and corn starch and evaluated some of their physical characteristics in greater detail. The properties of the molded products or cast films from amylopectin and starch esters were found to be generally unsatisfactory, consistent with the work of Mullen and Pacsu. On the other hand, it was found that the amylose esters could be molded quite easily at elevated temperatures and pressures, with reasonably strong and tough products; these esters also gave satisfactory films upon casting from solution. Wolff et al. also observed that the melting points of amylose esters were higher than that of their amylopectin counterparts, with the respective whole starch esters falling in between. It was also seen that the esters were amorphous as prepared, but heating the amylose esters, or orienting them by stretching at an elevated temperature, resulted in some crystallinity as detected by x-ray diffraction. (In fact, properties of fibers prepared from amylose triacetate were found to be significantly improved by secondary drawing (Whistler and Richards 1958, Wolff 1958) presumably due to increased crystallinity.) The ultimate tensile strength of fatty acid esters of amylose decreased with increasing length of the acyl group, a trend similar to that observed for cellulose. However, the amylose esters were found to be consistently weaker than the respective cellulose esters. The ultimate tensile extension of these derivatives displayed a fluctuating, but generally increasing trend. The water permeability of the amylose esters also decreases with increasing size of the ester group, which is attributable to the higher hydrophobicity of the higher esters (Gros and Feuge 1962). Mixed esters of amylose were also found to be promising in terms of manipulation of their physical and chemical properties (Wolff et al. 1957). This body of literature suggested that the properties of pure amylose esters approach those of the cellulose esters, but the properties of the esters based
on unfractionated starches were clearly inferior to their cellulose counterparts. This was attributed to the presence of a significant amount of branched amylopectin present in most commercial starches (for example, up to 70% or 100% in corn starches). For this reason, industrial utilization of highly substituted starch esters was deemed undesirable; amylose esters did show some promise but the high costs of amylose fractionation from starch precluded its use as a raw material for derivatization, especially given its lack of advantage over cellulose.

However, the increasing emphasis on environmentally degradable polymers coupled with recent work indicating that highly substituted polysaccharides can be degraded (albeit slowly) in the natural environment under the action of microorganisms (Buchanan et al. 1993, Komarek et al. 1993) has caused a renewed interest in starch derivatives. Among the various derivatives of starch, starch esters probably merit the closest re-examination since they seem to be suitable candidates for potentially replacing non-degradable thermoplastics for certain applications. Keeping in mind the past work in this area, it seems clear that amylopectin is undesirable as a fraction in the starch due to its adverse impact on mechanical and physical properties of these derivatives. Pure amylose seems to be the most desirable precursor for the starch-ester-based thermoplastics, though the expensive steps involved in the fractionation and purification of amylose would add substantially to the cost of these materials. However, a compromise is offered by the availability of high-amylose varieties of starch that contain dominant fractions of amylose. Utilization of these raw starch materials could provide suitable properties for the resulting esters, yet the high amylose content should obviate the need for any major purification steps. Moving along this line of thought, this work focuses on fatty acid esters of a high-amylose starch. C₄ - C₆ esters were utilized in this study, since they have been shown to be easily moldable, and reasonably tough as opposed to the more brittle lower esters. The
esters were prepared by an acid chloride reaction route. Subsequently, the thermal and mechanical properties of the neat and plasticized esters were evaluated.

3.2 Experimental

3.2.1 Preparation of Esters

The basic material used in this study was a purified high-amylose starch (Sigma Chemical Co., A-7043), consisting approximately of 70% amylose, and 30% amylopectin. The esterification of this starch was carried out by the method of Gros and Feuge (1962). This method was used in preference to the others reported in literature, since it allowed a larger scale of synthesis, with almost complete derivatization, and was claimed to lead to minimal degradation. The general method of synthesis was as follows: 0.1 mole of starch (on a repeat unit basis, i.e., 16.2 grams) was dried overnight in a vacuum oven at about 80 °C to minimize its moisture content. This starch was then placed in an Erlenmeyer flask, and 200 ml. of dioxane and 50 ml. of pyridine were added. This flask was then placed in an oil bath at 100 °C, with a magnetic stirrer being used for continuous vigorous mixing. 200 ml. of toluene mixed with 0.45 moles of the corresponding acid chloride was then added to the flask. The flask was sealed after fitting it with a condenser, and flushing it with nitrogen. The reaction was allowed to continue for 6 hrs. at constant temperature.†

While allowing the reaction mixture to cool down, part of the volatiles were removed by stripping under low pressure. After the remaining mixture had cooled down, it was poured with vigorous stirring into a dish containing a mixture of ethanol and ice-water. The derivatized starch (generally yellowish in color, probably partly due to pyridine impurities) eventually floated to the surface, and was removed subsequently. To purify the

† Under prolonged storage, dioxane can form peroxides which can be unstable; the acid chlorides can react with moisture in the air. Therefore, care was taken to use fresh reagents in the experiments.
polymer, it was immersed in an ethanol bath for a few days, and finally washed thoroughly with hot water. (The ethanol, though not a solvent for these esters, does swell them.)

These materials were utilized as such in the rheological studies, while thin films of the samples were cast from suspension of these polymers in chloroform for all the other studies. For plasticized samples, dibutyl phthalate (10% by weight of the polymer) was added to the solution before casting. The cast films were placed in an air stream for at least 48 hours before all testing to allow the residual solvent to evaporate.

3.2.2 Characterization of the Esters

The extent of the derivatization was measured using elemental analysis to obtain the carbon and nitrogen content of the product, as well as by saponification according to the alcoholic alkali saponification procedure described by Genung and Mallatt (1941). This latter procedure was as follows: 0.5 grams of the dried ester were placed in a 250 ml. Erlenmeyer flask. 20 mls. of a 0.5N sodium hydroxide solution in 90% ethanol were added, followed by 20 mls. of neat ethanol. The flask was then sealed and left aside for 24 hours at room temperature. Subsequently, the excess alkali was back-titrated with 0.25N hydrochloric acid, using phenolphthalein as an indicator. A slight excess of the acid was added, and the excess alkali was allowed to soak out for 4 hours. At the end of this period, the excess acid was titrated to neutrality with 0.5 N sodium hydroxide. Genung and Mallatt suggest that this method is preferable to the Eberstadt method, since it is not limited to lower aliphatic esters (unlike the latter).

3.2.3 Rheological Measurements

The rheological measurements on the blends were obtained with a capillary viscometer (Instron Model 3210 Rheometer coupled with a Model 4505 series Universal
Testing Instrument) using a procedure similar to that described in section 2.2.3. The rheology of each of the esters was measured at three temperatures in order to get an estimate of their flow activation energy.

3.2.4 Thermal Analysis

The calorimetric studies on the neat and plasticized esters were carried out on a differential scanning calorimeter (Perkin Elmer DSC 7 with sub-ambient operation capability). The tests were carried out on about 5-10 mg. of the sample (cast films) placed in standard crimpable aluminum pans. The first heat for the samples was initiated at -10 °C at a heating rate of 10 °C/min. At the end of the heating run, the sample was cooled at a rate of 10 °C/min. until the temperature of the sample was brought down back to -10 °C, at which point the second heat was initiated (with the same parameters as the first heat). Additional runs were also carried out with just the first heat for most samples, as were some simple annealing experiments for the un塑料ized esters.

3.2.5 Dynamic Mechanical Analysis

The tensile dynamic mechanical analyses were carried out on a Seiko DMS 200 instrument. Films of the neat and plasticized esters of thickness 0.2-0.3 millimeters, cut to a width of 0.6-0.7 mm approximately, were utilized in the testing (thinner samples tended to slip from the grips). The distance between the grips was set at 10 or 15 mm, depending upon the cross-sectional area of the sample such that the ratio of the testing length to the film cross-sectional area was at least 5. The amplitude of the elongation was 5 microns, and the measurements were made at frequencies of 1, 2, 5, and 10 Hz. The testing was initiated at -100 °C with the temperature being ramped up at 2 °C/min.; the test was
continued until failure or significant necking of the sample. This generally happened in the
region of 80-120 °C for the unplasticized esters, and 60-100 °C for the plasticized films.

3.2.6 Mechanical Testing

For the tensile mechanical testing, films of the esters (both plasticized and
unplasticized) of thickness of the order of 0.1-0.2 mm were utilized. Strips of the films
were cut using a razor blade; these strips were then mounted on rectangular cardboard
frames using cyanoacrylate adhesives or epoxy (the former is preferable since it is less
viscous and easily spreads; however, the cyanoacrylate ester monomer seemed to dissolve
the starch butyrate). For the testing, the frames were held at the top and bottom in
pneumatic grips such that the length of the polymer strip was along the direction of
extension. Subsequent to this, lateral cuts were made in the vertical sides of the frame,
such that the load would be borne only by the sample during the tensile testing. The
eventual testing was carried out at a constant rate of grip separation on an Instron Model
4505 Universal Testing Machine, with a load cell of 2000 g. The data were collected using
the Instron Mechanical Testing Series IX program, and reanalyzed using a graphics
program (Kaleidagraph 3.0.1, Abelebeck Software) to account for the initial variations in
the stress due to any slight mis-orientation or slack in the films. The nominal gauge length
of the samples was 25.4 mm, and the extension rate was 2.54 mm/min. for the modulus
determination (as indicated in ASTM D 882-91). Grip speeds of 2.54 and 12.7 mm/min.
were used to examine the ultimate tensile strain, and maximum nominal stress values as a
function of the strain rate. At least five specimens were utilized for measurements at each
condition.
3.2.7 Blending of Starch Esters and Starch

The starch butyrate prepared previously was powdered and mixed with an equal weight of high-amylose starch powder (about 25 grams each). This mixture was slowly fed through a funnel into the feeder of a single-screw Banbury mixer. The processing temperature was 170 °C at a screw speed of 25 RPM. The extrusion mixing proceeded quite smoothly, and the extruded material was fed through the mixer a second time to ensure good mixing.

An attempt to blend starch butyrate with Hylon VII pellets (HY 100, prepared at Novon) was also carried out. The screw speed was maintained at 25 RPM, but the temperature for this experiment was varied between 170 °C and 190 °C.

3.3 Results and Discussion

After purification, the esters were white or slightly off-white in color. As mentioned earlier, these esters do not form true solutions in solvents such as trichloroethylene, chloroform, and trichloroethane, but result in stable suspensions instead. This has also been noted by a number of other workers for various higher amylose esters (e.g., Mullen and Pacsu 1942, Gros and Feuge 1962).

The films of the starch butyrate ester were quite smooth and lustrous, and very stiff. However, these films were also very brittle, and displayed easy and rapid crack propagation. The starch valerate and hexanoate films were less shiny and slightly less brittle by comparison, but sometimes these (especially if the films were thicker, approximately \( \geq 0.3 \) mm) also exhibited a tendency to snap while being bent or cut. Addition of the dibutyl phthalate plasticizer resulted in a significant increase in the pliability of all the starch ester films, though the plasticized butyrate ester was still noticeably stiffer than the other two plasticized esters.
3.3.1 Extent of Conversion

The results from the elemental analysis and the alcohol alkali saponification procedure matched reasonably (Table 3.1), although the alcoholic alkali saponification procedure indicates slightly higher levels of conversion. In any case, these results indicate that almost complete conversion was reached for all the three esters. The low level of nitrogen present in the sample (presumably from the pyridine used as the catalyst in the reaction) indicates that the sample was quite well-purified.

Table 3.1: The degree of substitution of the starch esters as determined by elemental analysis, and by alcoholic alkali saponification.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Elemental Analysis</th>
<th>Saponification</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Carbon (wt %)</td>
<td>Nitrogen (wt %)</td>
</tr>
<tr>
<td>Starch Butyrate</td>
<td>57.9</td>
<td>0.16</td>
</tr>
<tr>
<td>Starch Valerate</td>
<td>60.4</td>
<td>0.05</td>
</tr>
<tr>
<td>Starch Hexanoate</td>
<td>62.8</td>
<td>0.16</td>
</tr>
</tbody>
</table>

3.3.2 Rheological Behavior

The rheological measurements for the starch esters are shown in Figures 3.1a - c. The shear rate vs. melt viscosity data indicate that, for the range of shear rates covered by the capillary viscometer, the molten esters are in the power-law regime (similar to that for the pure starches and the starch-EVOH blends discussed in Chapter 2). It is only for the
starch hexanoate at 170 °C that the appearance of a possible constant-viscosity regime is seen (though it should be noted at these higher temperatures and the low shear rates, the viscosity of the starch hexanoate melt is very low, and the shear stress is at the limits of experimental measurements achievable with the capillary rheometer). The melt viscosity of the starch butyrate is quite high, but still much lower than that of the HY 100 pellets (see Chapter 2); the overall magnitude of the viscosity is close to that of the NC 100 pellets, though the slope of the curve is closer to that of the WM 100. Furthermore, as the size of the hydrophobic side group is increased, for any given shear rate at a given temperature, the melt viscosity drops quite dramatically. The slopes of the melt viscosity vs. shear rate plots for the butyrate and valerate esters are close to each other, though greater than that of the hexanoate ester. Since the derivatization procedure was the same was for the three esters, we can assume that the amount of degradation of the starch during the reaction is similar. This would indicate that the changes in the behavior of the esters melts (especially the gross differences in their viscosities) is mainly attributable to the internal plasticization provided by these esters, as well as due to the changes in the conformation of the starch molecules caused by these bulky side groups.

The viscosity, \( \eta \), of plasticizer-containing starches has been found to have power law dependency on the shear rate, \( \dot{\gamma} \), and an Arrhenius dependence on the temperature, \( T \) (Villar 1994). (Studies have also showed a dependence on the moisture content, but that is not relevant for these hydrophobic ester.) The general form of this relationship is:

\[
\eta = m \dot{\gamma}^{(n-1)} \exp(\Delta H / RT)
\]

where \( m \) is the consistency index, \( n \) is the power-law exponent, and \( \Delta H \) is the flow activation energy. In our case, since the measurements indicated that we were operating in
the power-law regime, the flow activation energy could be obtained from a series of measurements at different temperatures for the same material. The average values of the flow activation energy for the three esters are shown in Table 3.2, along with some representative values for plasticized pure starches (data for latter taken from Villar 1994). It can be seen that the overall values of the flow activation energy of the starch esters do not change much with plasticization. The values are also close to those of HY 100, a modified high-amyllose starch quite similar to the starch precursor for our derivatization reaction. However, it is probably not advisable to draw any conclusions beyond such general comparisons, especially since the HY 100 pellets contained significant amounts of glycerin and water (as reported in Chapter 2) whereas the starch derivatives are plasticized internally by the hydrophobic esters groups.

Table 3.2: Flow activation energy for starch esters, and for some plasticized, unmodified starches.

<table>
<thead>
<tr>
<th>Sample</th>
<th>ΔH/R (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starch Butyrate</td>
<td>5480</td>
</tr>
<tr>
<td>Starch Valerate</td>
<td>4750</td>
</tr>
<tr>
<td>Starch Hexanoate</td>
<td>5350</td>
</tr>
<tr>
<td>HY 100</td>
<td>4250</td>
</tr>
<tr>
<td>NC 100</td>
<td>4360</td>
</tr>
<tr>
<td>WM 100</td>
<td>11700</td>
</tr>
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</table>
3.3.3 Thermal Behavior

The data for the neat and plasticized starch esters are given in Table 3.3, while the salient features of the thermal behavior of the neat and plasticized starch esters are best illustrated by the DSC plots for starch valerate shown in Figure 3.2. The starch valerate and hexanoate esters were found to display an endothermic peak (at about 124 and 92 °C respectively), though the starch butyrate does not display any endotherm. Other studies in literature on pure amylose esters have indicated the presence of some crystallinity for all three of these derivatives. In addition, the melting point observed in our studies are lower than the ones reported for the pure amylose counterparts (Cowie et al. 1969, Zugenmaier and Stenmeier 1986). These differences between our starch esters and those based on pure amylose may be attributable to the long-chain branching in the amylose fraction in our sample, and the presence of a significant fraction (∼30%) of amyllopectin. This should lead to a reduction in the ability to form crystals, as well as the formation of less perfect crystals. It is also possible that the butyrate ester does not provide enough of an internal plasticization to allow crystal formation during the casting of films from solution. It was also found that the crystalline structure does not reappear in the second heat of our heat-cool-heat experimental cycle. However, annealing (subsequently to melting) at temperatures above the glass transition point, and below the melting point led to reappearance of the starch valerate and hexanoate endotherms.

The glass transition temperatures for these materials also display a curious behavior. For the first heat, the glass transitions for films of the unplasticized esters (cast from solution) display two distinct glass transitions close to each other, the one at the higher temperature generally also being of a larger magnitude. As with the melting points, the glass transition temperatures for our esters are lower than those reported by Cowie et al. (1969) for the corresponding amylose esters. It is possible that the derivatized
<table>
<thead>
<tr>
<th>Sample</th>
<th>First Heat $T_{g1}$ (°C)</th>
<th>$T_g$ (°C)</th>
<th>Melting Point (°C)</th>
<th>Second Heat $T_{g2}$ (°C)</th>
<th>$T_g$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starch Butyrate</td>
<td>74</td>
<td>48</td>
<td>117</td>
<td>124</td>
<td>42</td>
</tr>
<tr>
<td>(Plasticized)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Starch Butyrate</td>
<td>39</td>
<td>64</td>
<td>95</td>
<td>42</td>
<td>41</td>
</tr>
<tr>
<td>(Plasticized)</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Starch Valerate</td>
<td>117</td>
<td>91</td>
<td>95</td>
<td>72</td>
<td></td>
</tr>
<tr>
<td>(Plasticized)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Starch Hexanoate</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Plasticized)</td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>
amylopectin and amylose molecules might be phase-separating to some extent in the cast films. Given that the (almost) linear amylose molecules have an architecture very different from the amylopectin (the latter composed almost exclusively of branches, generally only 15-30 repeat units long), there could very well be a difference in their glass transition temperatures. However, this cannot be proved conclusively from these data, and further experiments to test this hypothesis were not carried out at this time. In the second heat, in contrast, only one glass transition was observed for the esters at a temperature close to the larger transition observed in the first heat.

In comparison to the neat esters, the plasticized esters displayed smaller, and much broader transitions (see Fig. 3.2b). Since these transitions almost abutted each other, it was difficult to interpret them as clearly as for the neat esters. The lower temperature transition was attributed to a broad, single glass transition, and the second transition to a broad melting endotherm. (During the second heat, the melting endotherm was preceded by what seemed to be a small crystallization exotherm.). The behavior of the plasticized esters was also different from that of the neat esters in that the sequence of melting, cooling and subsequent re-heating generally resulted in the reappearance of the endotherm at about the same peak temperatures as the first heat. The temperatures of these transitions could be estimated only in a very rough fashion, given their broad, smeared nature. The overall data seems to indicate that large fraction of the plasticizer seems to allow enough molecular mobility for some crystallization, but is also responsible for smearing the transitions. The difference between the glass transition temperatures observed in the first and second heat of the plasticized esters could possible be due to some aging effect (such as some phase separation between the plasticizer and polymer) since the films were utilized in tests a few days after they were cast. This might also be responsible for the variations sometimes observed between different runs for the same plasticized esters.
3.3.4 Dynamic Mechanical Behavior

Figures 3.3a - e show the storage modulus ($E'$) and the loss factor (tan $\delta$) data for the neat and plasticized starches. The highest temperature at which the tan $\delta$ peak appears is reported as the DMA $\alpha$-transition (or the glass transition temperature); the second (local) maximum observed in the tan $\delta$ curves at a lower temperature is reported as the DMA $\beta$-transition (probably due to some side-chain motions).

For the neat esters, it can be seen that the $\alpha$-transition temperature moves to lower temperatures, and the corresponding tan $\delta$ peak becomes broader as the size of the esters group is increased. The $\alpha$-transition temperatures are slightly higher than that for the larger glass transition in the DSC first heat ($T_{g1}$), although it should be noted that the heating rate during the DMA was much lower than that in the DSC experiment. A sharp drop in $E'$ coincides with the tan $\delta$ peak, which is as expected for these mainly amorphous polymers. The $\beta$-transition is much less prominent, although for the higher neat esters, the presence of this transition is clear at a temperature of about -45 °C.

For the plasticized starches, the $\alpha$-transition shifts to a much lower temperature, as expected, and the peak is also much broader, consistent with the observations on the DSC. Also, for these materials, there is no sharp drop in $E'$ at any temperature, just a gradual decline. Compared to the neat esters, however, the plasticized esters show a significant drop in $E'$ at almost all temperatures as expected (except at very low temperatures where the plasticizer presumably cannot contribute to chain motion). The $\beta$-transition peak also becomes much more pronounced with the addition of plasticizer, though it does not significantly shift position on the temperature axis.

The transition temperatures at the lowest measured frequency (i.e., 1 Hz), and the values of $E'$ at 2 Hz (and corresponding to a temperature of 21 °C) are reported in Table 3.4. ($E'$ is tabulated for the measurement at 2 Hz, since this corresponds the closest to a
strain rate of 0.1 min⁻¹ which is the strain rate used for the modulus measurements on the Instron. Also, the tensile testing on the Instron was carried out at 21 °C, and therefore, the value of E' is reported for this temperature to allow comparison between the modulus values from the DMA and the Instron.)

Table 3.4: Transition temperatures (1 Hz), and the storage modulus, E' at 21 °C (2 Hz), for the neat and plasticized (10% DBP by weight) starch esters as obtained by tensile dynamic mechanical analysis.

<table>
<thead>
<tr>
<th>Sample</th>
<th>α Transition (°C)</th>
<th>β Transition (°C)</th>
<th>E' (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starch Butyrate</td>
<td>85</td>
<td>-44</td>
<td>736</td>
</tr>
<tr>
<td>Starch Butyrate (Plasticized)</td>
<td>56</td>
<td>-33</td>
<td>310</td>
</tr>
<tr>
<td>Starch Valerate</td>
<td>77</td>
<td>-50</td>
<td>488</td>
</tr>
<tr>
<td>Starch Valerate (Plasticized)</td>
<td>35</td>
<td>-43</td>
<td>83.3</td>
</tr>
<tr>
<td>Starch Hexanoate</td>
<td>65</td>
<td>-48</td>
<td>243</td>
</tr>
<tr>
<td>Starch Hexanoate (Plasticized)</td>
<td>33</td>
<td>-44</td>
<td>42.3</td>
</tr>
</tbody>
</table>
3.3.5 Mechanical Properties

Table 3.5 lists the numerical values of the mechanical properties for the neat and plasticized esters, and Figures 3.4a - e show representative stress-strain curves for these materials. Addition of the ester group modifies the mechanical properties of the starch significantly as mentioned earlier. This can be attributed to the internal plasticization provided by the ester groups. The tensile mechanical tests on these materials showed the general expected trends in the response of these materials, but also showed some unexpected results at the lower strain rate. At the lower strain rate, the neat starch hexanoate displayed the formation of a stable neck that propagated with increasing strain. The starch valerate also formed a neck, which however did not propagate; the localized neck resulted in comparatively early failure. The behavior of the butyrate ester was contrary to expectation, though. These samples necked significantly, and displayed strain-to-break values larger the valerate samples.

The plasticized samples all necked clearly, but their overall extensibility was not very different from that of their neat counterparts. The plasticized samples, however, failed due to the propagation of cracks from the edges of the film as it was pulled. It is not clear if these cracks were initiated from flaws formed during the cutting of the films. In any case, the plasticized films did not seem to show much tear resistance. A wide variation in the strain-to-break values for different specimens for any given material was generally also seen, leading to the larger ranges indicated in Table 3.5.

At the higher strain rate, the behavior of the neat esters changed significantly. The starch butyrate samples displayed an almost brittle failure, and shattered at comparatively low strains. The valerate esters necked locally and then fractured shortly thereafter as the test proceeded. The starch hexanoate also necked, but in a more stable fashion, allowing a reasonable extension before failure. Overall, the neat starch butyrate showed the greatest

122
<table>
<thead>
<tr>
<th>Sample</th>
<th>Initial Modulus (MPa)</th>
<th>Strain Rate = 0.1/min.</th>
<th>Ultimate Strain (percent)</th>
<th>Strain Rate = 0.5/min.</th>
<th>Maximum Nominal Stress (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starch Butyrate</td>
<td>594±15</td>
<td>36.7±23</td>
<td>7.33±4.3</td>
<td>17.9±2.5</td>
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<tr>
<td>Starch Butyrate (Plasticized)</td>
<td>275±14</td>
<td>40.9±5.4</td>
<td>6.60±0.1</td>
<td>9.86±0.7</td>
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</tr>
<tr>
<td>Starch Valerate</td>
<td>495±17</td>
<td>20.2±4.8</td>
<td>12.7±0.6</td>
<td>14.1±0.7</td>
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</tr>
<tr>
<td>Starch Valerate (Plasticized)</td>
<td>93.7±12</td>
<td>44.4±17</td>
<td>2.72±0.2</td>
<td>3.17±0.2</td>
<td></td>
</tr>
<tr>
<td>Starch Hexanoate</td>
<td>191±16</td>
<td>74.9±36</td>
<td>5.48±0.3</td>
<td>8.10±1.2</td>
<td></td>
</tr>
<tr>
<td>Starch Hexanoate (Plasticized)</td>
<td>52.8±15</td>
<td>59.2±18</td>
<td>1.75±0.3</td>
<td>1.50±0.2</td>
<td></td>
</tr>
</tbody>
</table>
dependence upon the strain rate. The plasticized esters, on the other hand, showed a much smaller sensitivity to the strain rate; in fact, they displayed a slight increase in the values for the ultimate tensile strains as compared to those for the lower strain rate.

The values for the initial tensile modulus for the neat and plasticized esters indicate that, as expected, plasticization causes a significant drop in the modulus of the esters. The overall trends and values also correspond well with those obtained from the DMA. The mechanical tests also indicate that the maximum nominal stress for these starch derivatives drops monotonically with increasing size of the ester group, and also with plasticization. Both the neat and the plasticized starches generally displayed an increase in the maximum nominal stress at the higher strain rate (except for the plasticized starch hexanoate).†

3.3.6 Blending Experiments

In the blending of the starch butyrate with the powdered starch, the final extruded material appeared quite uniform with a light brown color and was quite hard; overall, the two components seemed well mixed. Part of this extrudate was placed in water to test its stability in aqueous medium; the material was very stable, and maintained its shape and strength, over a period of months. This indicates that the starch butyrate was probably the continuous phase in the blend with the unmodified starch forming a dispersion in the matrix provided by the ester.

The attempt to mix the starch butyrate with the HY 100 pellets was not as successful, probably because the temperature was insufficient to melt the starch pellets. (The preparation of these pellets at Novon employed much higher pressures and plasticizer contents, conditions which allow the melt-processing of this starch.) Increasing the

† The nominal stress, i.e., the load per unit initial cross-sectional area, and nominal strain, i.e., extension relative to overall initial length, are reported here since the specimens neck locally during the test leading to non-uniform strain over the sample. The films were too thin to mount strain gauges to measure real strains. Therefore, it was not possible to estimate the true stress and strain in the polymer as the test proceeded.
extrusion temperature to 190 °C did not improve the mixing between the feed materials. Consequently, the appearance of the extrudate was extremely inhomogeneous; the HY 100 pellets just seemed to be embedded in a matrix of the starch ester.

3.4 Conclusions

As with pure amylose, chemical modification of high-amylose starch with fatty acid esters is achievable through dispersion in an inert solvent and by reaction with the appropriate acid chloride in the presence of pyridine. The resulting starch esters are hydrohobic, thermoplastic materials that can be shaped, handled and processed with much greater ease than the starch precursor. At least some of the higher esters of high-amylose starch (such as the valerate and hexanoate) are semi-crystalline. These materials possess reasonable mechanical properties in terms of their tensile modulus and load carrying capacity, although their ultimate tensile extension is much lower than commodity thermoplastics such as polyolefins. (Mechanical tests on the neat starch esters indicate elastic modulii ranging from 200 to 600 MPa, maximum nominal stress from 5 to 18 MPa, and ultimate tensile strain from 10 to 75% as we span the range from starch butyrate to starch hexanoate. In comparison, for example, representative values of these parameters for low density polyethylene (LDPE) are as follows: tensile modulus ranging from 55 to 172 MPa, tensile strength from 15 to 79 MPa, and elongation at break from 150 to 600% (Quirk and Alsamarraie 1989). The starch esters are also quite susceptible to propagation of cracks, and therefore their tear strength is low. The unplasticized butyrate ester seems to be too brittle to use neat, though the addition of plasticizer does ameliorate the situation somewhat. The unplasticized starch valerate and hexanoate films were less brittle than their butyrate counterpart; plasticization rendered them more flexible. It is conceivable that such higher esters of high-amylose starch could eventually find use in some applications where
biodegradability is required, but the mechanical property requirements are not very demanding.

The mixtures of esters and unmodified starches also seems to be promising, especially since the addition of the unmodified starch should serve to lower the cost as well as enhance the degradability of the final product. However, it seems that successful mixing of unmodified starches and starch esters will probably require the utilization of finely powdered starch such that the product will have a uniform dispersion of small starch particles in the thermoplastic ester phase (rather than large discrete pellets).
Fig. 3.1: Melt viscosity as a function of shear rate for high-amylose starch esters:
(a) Starch hexanoate
Fig. 3.1: (b) Starch valerate
Fig. 3.1: (c) Starch butyrate
Fig. 3.2: Thermal behavior of the neat and plasticized starch esters illustrated by the DSC plots for (a) Starch valerate - neat
Fig. 3.2: (b) Starch valerate - plasticized
Fig. 3.3: DMA data for neat and plasticized starch esters: (a) Starch butyrate - neat, (b) Starch butyrate - plasticized
Fig. 3.3: (c) Starch valerate - neat

Fig. 3.3: (d) Starch valerate - plasticized
Fig. 3.3:  (e) Starch hexanoate - neat

Fig. 3.3:  (f) Starch hexanoate - plasticized
Fig. 3.4: Representative nominal stress vs. strain curves for neat and plasticized esters:
(a) Starch butyrate; strain rate 0.1/min.
(b) Starch butyrate; strain rate 0.5/min.
Fig. 3.4:  (c) Starch valerate; strain rate 0.1/min.

Fig. 3.4:  (d) Starch valerate; strain rate 0.5/min.
Fig. 3.4: (e) Starch hexanoate; strain rate 0.1/min.

Fig. 3.4: (f) Starch hexanoate; strain rate 0.5/min.
The natural biodegradability of starch has resulted in a variety of attempts to utilize it as a component of thermoplastic blends to enhance their biodegradability. When mixed in its granular form with thermoplastics, starch acts as a non-reinforcing biodegradable filler since there is no mechanism of stress transfer across the interface of the starch granule and the thermoplastic matrix. Although chemical derivatization of starch has shown some success in improving the properties of such blends, modification of starch by chemical means is an often cumbersome step, and can significantly increase the costs of such blends.

Part of this thesis shows that physical modification of starches by ionizing electron beam irradiation, a process that lends itself easily to large-scale commercial applications, can allow manipulation of the blend microstructure, and hence the eventual properties of the material. Tensile tests indicated that the stress- and strain-to-break values of filaments obtained from irradiated blend pellets can be significantly higher than the filaments obtained from control blends. The results were the most striking for blends containing 40-50% of amylopectin-containing starches. (For example, the stress- and strain-to-break for WM 50 increased, relative to the controls, by approximately 30% and 50% respectively for the filaments from irradiated pellets.) These changes in the mechanical properties have been attributed to the significant reduction of inter- and intra-molecular forces in starches by the radiation, enhancing the mobility of the starch molecules in the blend melt, which in turn can allow the formation of a different microstructure. As observed by ESEM, the filaments prepared from 50/50 blends containing irradiated starches of high amylopectin content have almost co-continuous starch and EVOH phases, as opposed to the control filaments where the starch seems to be in discrete domains embedded in a continuous EVOH matrix.
Such an irradiation-based modification of starches for eventual blending with thermoplastics might be of use in order to tailor the properties of the blend. However, a number of issues are raised by this work that could form the basis of future investigations to allow a better understanding and eventual optimization of such a process. Effects of various radiation parameters such as the dose rate, the overall dose, and the influence of the water content on the eventual fragmentation of the starch could be studied. It might be interesting to focus mainly on the high-amylopectin content such as the native corn since they offer the most favorable economics. The microstructure of blends containing irradiated starches could also be studied in greater detail, especially since the morphological investigation in this work, although brief, indicated some very interesting changes in the structures of these blends.

It would also be useful to study the properties of blends prepared directly from irradiated starches and thermoplastics (instead of the cumbersome two-step process followed here). In addition, since chemical modification of starch can also be carried out using appropriate monomers (such as vinyl-containing monomers), it might be also of interest to explore the potential of irradiation-based physical and chemical modification of starches in the same step.

The second major part of this thesis involved extensive chemical modification of starches to render them more processable, to improve their physical properties, and to reduce the sensitivity of these properties to ambient humidity levels (these being the major stumbling blocks to the use of pure starch as a biodegradable thermoplastic). The higher fatty acid esters of starch offer a reasonably straightforward route to impart these properties, with these derivatives being hydrophobic and lower melting than their starch precursors. Preparation and characterization of a series of these derivatives of high-amylose starch indicated that these materials are thermoplastic (and some of them being
semi-crystalline). The mechanical and other physical properties of these high-amylose starch esters could be adequate for some commodity applications, although in general terms these materials do not compare favorable with commodity thermoplastics, especially in terms of ductility (the neat starch esters have ultimate tensile strains ranging from about 10 to 75%, whereas polyolefins such as low density polyethylene and polypropylene often have ultimate tensile strain values of a few hundred percent). As might be expected, plasticization enhances the ductility of the starch esters somewhat, but this is manifested more at higher strain rates. Therefore it is unlikely that these starch esters will be able to replace thermoplastics currently in use. However, for applications where biodegradability is an overriding concern and material performance is not a critical issue, starch esters might find some use.

It might be of use to further investigate certain aspects of this chemical derivatization approach that could allow better tailoring of the properties of these derivatives. Of special interest might be properties of mixed esters such as the acetate-butyrate, as well as the effects of different kinds and different levels of plasticizers upon the properties of such and other esters. It should also be useful to study the effect of the molecular weight of the precursor starch upon the rheological and mechanical properties of their fatty acid esters. The limited efforts to blend starch esters and neat starch displayed some modest success; therefore, blending experiments to mix starch esters and neat starch also offer an interesting direction for future investigations. In this context, it could be especially interesting to combine the two different aspects of this thesis; i.e., prepare and characterize the blends of irradiation-modified starch with starch esters.

In the end, however, the utilization of starch as the basis of or as a component of commodity thermoplastic materials depends upon the demand for environmentally degradable materials, whether this is created by regulations or by consumer preferences. If
that does come about, one could envisage that some of the explorations in this thesis might merit a revisitation much in the same way that part of this thesis of starch entailed revisiting many aspects of starch technology from years past.
Table A1.1: Composition and processing parameters for the secondary series of starch/EVOH blends.

<table>
<thead>
<tr>
<th>Nomenclature</th>
<th>Starch (dry wt%)</th>
<th>Final glycerin content (wt%)</th>
<th>Final water content (wt%)</th>
<th>Extruder peak temperature (°C)</th>
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<tr>
<td>Waxy Maize</td>
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<td>WM 85</td>
<td>85</td>
<td>13.9</td>
<td>8.8</td>
<td>185</td>
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<td>WM 60</td>
<td>60</td>
<td>14.2</td>
<td>6.6</td>
<td>180</td>
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<td>WM 40</td>
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<td>4.9</td>
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<td>Native Corn</td>
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<td>NC 85</td>
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<td>13.8</td>
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<td>180</td>
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Table A1.2: Detailed DSC data on EVOH and 50/50 blends (all containing glycerin and water as noted in Table 2.2); (a) EVOH

<table>
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<tr>
<th>Sample</th>
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<td>$T_{peak}$</td>
<td>$\Delta H$</td>
<td>$T_{onset}$</td>
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<td>EVOH Pellets</td>
<td>128.9</td>
<td>140.6</td>
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<td>111.4</td>
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<td>(Control)</td>
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<tr>
<td>EVOH Pellets</td>
<td>134.0</td>
<td>143.5</td>
<td>62.29</td>
<td>110.3</td>
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<td>(Irradiated, 200 kGys)</td>
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<tr>
<td>EVOH Filaments</td>
<td>129.1</td>
<td>139.5</td>
<td>48.91</td>
<td>114.9</td>
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<tr>
<td>(Control)</td>
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<tr>
<td>EVOH Filaments</td>
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<td>138.9</td>
<td>19.86</td>
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<td>(from irradiated pellets, 200 kGys)</td>
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### Table A1.2: (b) WM 50 blends

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<th>Cool</th>
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<tr>
<td></td>
<td>$T_{onset}$</td>
<td>$T_{peak}$</td>
<td>$\Delta H$</td>
<td>$T_{onset}$</td>
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<td>$T_{peak}$</td>
<td>$\Delta H$</td>
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<td>(°C)</td>
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<td>(J/g&lt;sub&gt;EVOH&lt;/sub&gt;)</td>
<td>(°C)</td>
<td>(°C)</td>
<td>(J/g&lt;sub&gt;EVOH&lt;/sub&gt;)</td>
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<td>(J/g&lt;sub&gt;EVOH&lt;/sub&gt;)</td>
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<tr>
<td>WM 50 Pellets (Control)</td>
<td>124.3</td>
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<td>100.7</td>
<td>94.5</td>
<td>50.65</td>
<td>128.7</td>
<td>137.4</td>
<td>46.25</td>
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<tr>
<td>WM 50 Pellets (irradiated, 200 kGys)</td>
<td>117.1</td>
<td>128.8</td>
<td>53.91</td>
<td>91.6</td>
<td>84.7</td>
<td>50.83</td>
<td>117.9</td>
<td>129.2</td>
<td>49.71</td>
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<td>WM 50 Filaments (Control)</td>
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<td>39.05</td>
<td>117.4</td>
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<td>59.87</td>
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<td>46.07</td>
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<td>47.61</td>
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<td>48.94</td>
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Table A1.2: (c) NC 50 blends

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<td>$T_{peak}$ ($^\circ$C)</td>
<td>$\Delta H$ (J/g$_{EVOH}$)</td>
<td>$T_{onset}$ ($^\circ$C)</td>
<td>$T_{peak}$ ($^\circ$C)</td>
<td>$\Delta H$ (J/g$_{EVOH}$)</td>
<td>$T_{onset}$ ($^\circ$C)</td>
<td>$T_{peak}$ ($^\circ$C)</td>
<td>$\Delta H$ (J/g$_{EVOH}$)</td>
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<tr>
<td>NC 50 Pellets (Control)</td>
<td>119.4</td>
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<td>109.2</td>
<td>109.2</td>
<td>53.01</td>
<td>136.0</td>
<td>144.0</td>
<td>45.09</td>
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<tr>
<td>NC 50 Pellets (Irradiated, 200 kGys)</td>
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<td>128.3</td>
<td>52.73</td>
<td>78.3</td>
<td>85.3</td>
<td>45.56</td>
<td>114.4</td>
<td>125.9</td>
<td>42.10</td>
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<td>NC 50 Filaments (Control)</td>
<td>123.0</td>
<td>132.6</td>
<td>52.78</td>
<td>94.1</td>
<td>99.1</td>
<td>49.69</td>
<td>124.2</td>
<td>133.9</td>
<td>41.92</td>
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<td>NC 50 Filaments (from irradiated pellets, 200 kGys)</td>
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<td>125.4</td>
<td>54.44</td>
<td>81.7</td>
<td>88.6</td>
<td>49.45</td>
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Table A1.2: (d) HY 50 blends

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<th>Sample</th>
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<th>Cooling</th>
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<tr>
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<td>$T_{peak}$</td>
<td>$\Delta H$</td>
<td></td>
<td>$T_{onset}$</td>
<td>$T_{peak}$</td>
<td>$\Delta H$</td>
<td></td>
<td>$T_{onset}$</td>
</tr>
<tr>
<td></td>
<td>(°C)</td>
<td>(°C)</td>
<td>(J/g EVOH)</td>
<td></td>
<td>(°C)</td>
<td>(°C)</td>
<td>(J/g EVOH)</td>
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<td>(°C)</td>
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<td>HY 50 Pellets (Control)</td>
<td>112.9</td>
<td>124.1</td>
<td>30.95</td>
<td></td>
<td>103.1</td>
<td>96.0</td>
<td>40.70</td>
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<td>123.7</td>
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<tr>
<td>HY 50 Pellets (Irradiated, 200 kGys)</td>
<td>109.6</td>
<td>122.2</td>
<td>43.59</td>
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<td>79.00</td>
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<tr>
<td>HY 50 Filaments (Control)</td>
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<td>128.1</td>
<td>38.00</td>
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<td>106.7</td>
<td>102.3</td>
<td>40.08</td>
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<td>125.5</td>
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<tr>
<td>HY 50 Filaments (from irradiated pellets, 200 kGys)</td>
<td>106.7</td>
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<td>81.75</td>
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Table A1.3: Tabulated mechanical properties of EVOH and starch/EVOH blends; (a) Irradiated filaments

<table>
<thead>
<tr>
<th>Sample</th>
<th>Diameter (µm)</th>
<th>Elastic Modulus (MPa)</th>
<th>Nominal Tensile Strength (MPa)</th>
<th>Ultimate Tensile Strain (percent)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EVOH (Control)</td>
<td>521.3±21.4</td>
<td>343.7±15.4</td>
<td>44.25±2.33</td>
<td>420.7±20.3</td>
</tr>
<tr>
<td>EVOH (20 kGys)</td>
<td>503.2±23.0</td>
<td>335.0±25.3</td>
<td>42.94±2.28</td>
<td>419.2±11.7</td>
</tr>
<tr>
<td>EVOH (40 kGys)</td>
<td>499.2±24.2</td>
<td>350.6±17.2</td>
<td>42.18±2.09</td>
<td>410.3±12.1</td>
</tr>
<tr>
<td>EVOH (80 kGys)</td>
<td>514.9±22.8</td>
<td>351.1±12.5</td>
<td>39.22±1.92</td>
<td>398.8±15.3</td>
</tr>
<tr>
<td>EVOH (120 kGys)</td>
<td>506.7±32.5</td>
<td>351.9±21.1</td>
<td>37.71±2.74</td>
<td>386.9±11.7</td>
</tr>
<tr>
<td>EVOH (160 kGys)</td>
<td>505.6±27.4</td>
<td>350.6±15.4</td>
<td>32.60±2.20</td>
<td>353.5±17.6</td>
</tr>
<tr>
<td>EVOH (200 kGys)</td>
<td>520.9±24.7</td>
<td>382.5±14.2</td>
<td>28.29±2.87</td>
<td>309.7±23.6</td>
</tr>
<tr>
<td>HY 50 (Control)</td>
<td>748.1±5.9</td>
<td>121.5±6.6</td>
<td>21.09±0.33</td>
<td>321.3±9.9</td>
</tr>
<tr>
<td>HY 50 (20 kGys)</td>
<td>741.2±7.6</td>
<td>112.9±4.8</td>
<td>19.08±0.62</td>
<td>303.4±10.6</td>
</tr>
<tr>
<td>HY 50 (40 kGys)</td>
<td>746.4±5.0</td>
<td>122.7±7.5</td>
<td>17.82±0.35</td>
<td>295.3±7.9</td>
</tr>
<tr>
<td>HY 50 (80kGys)</td>
<td>745.8±3.6</td>
<td>119.2±7.7</td>
<td>15.84±0.45</td>
<td>283.5±17.3</td>
</tr>
<tr>
<td>HY 50 (120 kGys)</td>
<td>745.4±3.4</td>
<td>120.4±6.9</td>
<td>14.42±0.42</td>
<td>269.6±15.5</td>
</tr>
<tr>
<td>HY 50 (160 kGys)</td>
<td>743.7±3.5</td>
<td>122.8±10.1</td>
<td>13.02±0.43</td>
<td>254.2±18.8</td>
</tr>
<tr>
<td>HY 50 (200 kGys)</td>
<td>747.6±3.9</td>
<td>116.1±6.4</td>
<td>11.64±0.49</td>
<td>228.7±26.6</td>
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</table>
Table A1.3: (a) Irradiated filaments (continued)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Diameter (µm)</th>
<th>Elastic Modulus (MPa)</th>
<th>Nominal Tensile Strength (MPa)</th>
<th>Ultimate Tensile Strain (percent)</th>
</tr>
</thead>
<tbody>
<tr>
<td>WM 50 (Control)</td>
<td>759.2 ± 49.7</td>
<td>217.9 ± 19.8</td>
<td>14.91 ± 0.40</td>
<td>246.0 ± 15.9</td>
</tr>
<tr>
<td>WM 50 (20 kGys)</td>
<td>834.7 ± 23.6</td>
<td>225.1 ± 22.8</td>
<td>14.99 ± 0.46</td>
<td>243.9 ± 23.0</td>
</tr>
<tr>
<td>WM 50 (40 kGys)</td>
<td>852.0 ± 30.6</td>
<td>256.3 ± 26.9</td>
<td>14.37 ± 0.42</td>
<td>217.1 ± 20.6</td>
</tr>
<tr>
<td>WM 50 (80 kGys)</td>
<td>855.3 ± 23.7</td>
<td>233.6 ± 33.3</td>
<td>14.19 ± 0.38</td>
<td>207 ± 16.2</td>
</tr>
<tr>
<td>WM 50 (120 kGys)</td>
<td>853.5 ± 21.8</td>
<td>238.7 ± 21.8</td>
<td>13.96 ± 0.29</td>
<td>196.2 ± 17.2</td>
</tr>
<tr>
<td>WM 50 (160 kGys)</td>
<td>845.6 ± 33.1</td>
<td>249.0 ± 25.1</td>
<td>13.67 ± 0.39</td>
<td>181.0 ± 37.1</td>
</tr>
<tr>
<td>WM 50 (200 kGys)</td>
<td>837.9 ± 22.9</td>
<td>220.9 ± 23.3</td>
<td>13.29 ± 0.51</td>
<td>191.17 ± 26.0</td>
</tr>
<tr>
<td>NC 50 (Control)</td>
<td>771.3 ± 22.9</td>
<td>135.1 ± 17.3</td>
<td>15.23 ± 0.50</td>
<td>267.6 ± 11.7</td>
</tr>
<tr>
<td>NC 50 (20 kGys)</td>
<td>771.5 ± 21.5</td>
<td>159.5 ± 21.0</td>
<td>14.49 ± 0.24</td>
<td>218.9 ± 14.2</td>
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<tr>
<td>NC 50 (40 kGys)</td>
<td>766.8 ± 11.8</td>
<td>156.25 ± 16.5</td>
<td>14.04 ± 0.49</td>
<td>225.0 ± 14.3</td>
</tr>
<tr>
<td>NC 50 (80 kGys)</td>
<td>773.9 ± 19.8</td>
<td>152.8 ± 18.7</td>
<td>13.28 ± 0.36</td>
<td>199.2 ± 15.8</td>
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<tr>
<td>NC 50 (120 kGys)</td>
<td>776.6 ± 22.4</td>
<td>160.0 ± 26.7</td>
<td>12.65 ± 0.63</td>
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<tr>
<td>NC 50 (160 kGys)</td>
<td>767.9 ± 27.1</td>
<td>145.5 ± 13.1</td>
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<td>167.6 ± 24.7</td>
</tr>
<tr>
<td>NC 50 (200 kGys)</td>
<td>764.1 ± 25.0</td>
<td>154.8 ± 19.0</td>
<td>11.65 ± 0.38</td>
<td>132.2 ± 37.8</td>
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</tbody>
</table>
Table A1.3: (b) Filaments from irradiated pellets

<table>
<thead>
<tr>
<th>Sample</th>
<th>Diameter (µm)</th>
<th>Elastic Modulus (MPa)</th>
<th>Nominal Tensile Strength (MPa)</th>
<th>Ultimate Tensile Strain (percent)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HY 15 (Control)</td>
<td>543.1±20.2</td>
<td>236.4±22.5</td>
<td>32.79±1.9</td>
<td>408.1±13.7</td>
</tr>
<tr>
<td>HY 15 (200 kGys)</td>
<td>613.0±19.1</td>
<td>233.8±10.2</td>
<td>29.5±0.9</td>
<td>404.3±11.9</td>
</tr>
<tr>
<td>HY 30 (Control)</td>
<td>694.7±4.2</td>
<td>192.6±15.3</td>
<td>27.5±0.5</td>
<td>355.6±20.0</td>
</tr>
<tr>
<td>HY 30 (200 kGys)</td>
<td>640.7±9.7</td>
<td>192.8±11.3</td>
<td>24.7±0.9</td>
<td>358.1±15.9</td>
</tr>
<tr>
<td>HY 40 (Control)</td>
<td>708.1±2.3</td>
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<td>22.89±0.77</td>
<td>327.3±16.7</td>
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<tr>
<td>HY 40 (200 kGys)</td>
<td>690.2±6.5</td>
<td>167.8±7.5</td>
<td>19.22±0.63</td>
<td>345.6±16.7</td>
</tr>
<tr>
<td>HY 50 (Control)</td>
<td>748.1±5.9</td>
<td>121.5±6.6</td>
<td>21.09±0.5</td>
<td>321.3±9.9</td>
</tr>
<tr>
<td>HY 50 (80 kGys)</td>
<td>713.7±7.2</td>
<td>126.2±7.1</td>
<td>17.63±0.59</td>
<td>319.5±10.7</td>
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<tr>
<td>HY 50 (200 kGys)</td>
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<td>HY 60 (Control)</td>
<td>742.8±5.0</td>
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<td>266.7±14.8</td>
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<tr>
<td>HY 60 (200 kGys)</td>
<td>736.8±2.8</td>
<td>195.2±6.1</td>
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<td>262.0±8.0</td>
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<tr>
<td>EVOH (Control)</td>
<td>521.3±21.4</td>
<td>343.7±15.4</td>
<td>44.25±2.33</td>
<td>420.7±20.3</td>
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<tr>
<td>EVOH (80 kGys)</td>
<td>522.5±17.2</td>
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<td>409.5±10.6</td>
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<tr>
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<td>561.6±16.0</td>
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Table A1.3: (b) Filaments from irradiated pellets (continued)

<table>
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<th>Sample</th>
<th>Diameter (µm)</th>
<th>Elastic Modulus (MPa)</th>
<th>Nominal Tensile Strength (MPa)</th>
<th>Ultimate Tensile Strain (percent)</th>
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</thead>
<tbody>
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<td>NC 15 (Control)</td>
<td>576.4±13.4</td>
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<td>408.4±8.3</td>
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<tr>
<td>NC 15 (200 kGys)</td>
<td>693.0±17.2</td>
<td>211.7±7.0</td>
<td>29.9±1.0</td>
<td>408.2±14.6</td>
</tr>
<tr>
<td>NC 30 (Control)</td>
<td>610.1±11.7</td>
<td>184.8±13.9</td>
<td>24.7±1.0</td>
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</tr>
<tr>
<td>NC 30 (200 kGys)</td>
<td>763.4±28.2</td>
<td>220.6±7.8</td>
<td>25.9±0.7</td>
<td>383.8±18.1</td>
</tr>
<tr>
<td>NC 40 (Control)</td>
<td>680.9±6.95</td>
<td>129.2±8.4</td>
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<td>NC 40 (200 kGys)</td>
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<tr>
<td>NC 50 (Control)</td>
<td>771.3±22.9</td>
<td>135.1±17.3</td>
<td>15.23±0.5</td>
<td>267.6±11.7</td>
</tr>
<tr>
<td>NC 50 (80 kGys)</td>
<td>826.9±20.1</td>
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<td>299.1±16.2</td>
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<tr>
<td>NC 50 (200 kGys)</td>
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<tr>
<td>NC 60 (Control)</td>
<td>717.9±20.6</td>
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<tr>
<td>NC 60 (200 kGys)</td>
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<td>5.94±0.77</td>
<td>359.5±30.4</td>
</tr>
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<td>NC 70 (Control)</td>
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<td>52.6±8.5</td>
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<tr>
<td>NC 70 (200 kGys)</td>
<td>739.6±6.5</td>
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<td>57.9±9.2</td>
</tr>
<tr>
<td>Sample</td>
<td>Diameter (µm)</td>
<td>Elastic Modulus (MPa)</td>
<td>Nominal Tensile Strength (MPa)</td>
<td>Ultimate Tensile Strain (percent)</td>
</tr>
<tr>
<td>-----------------</td>
<td>---------------</td>
<td>-----------------------</td>
<td>-------------------------------</td>
<td>----------------------------------</td>
</tr>
<tr>
<td>WM 15 (Control)</td>
<td>520.7 ± 14.2</td>
<td>227.0 ± 15.9</td>
<td>32.7 ± 1.2</td>
<td>421.4 ± 14.2</td>
</tr>
<tr>
<td>WM 15 (200 kGys)</td>
<td>785.7 ± 31.0</td>
<td>240.2 ± 7.3</td>
<td>31.0 ± 0.7</td>
<td>429.5 ± 7.5</td>
</tr>
<tr>
<td>WM 30 (Control)</td>
<td>598.8 ± 17.2</td>
<td>205.7 ± 17.1</td>
<td>25.1 ± 0.5</td>
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</tr>
<tr>
<td>WM 30 (200 kGys)</td>
<td>888.7 ± 11.6</td>
<td>235.7 ± 9.8</td>
<td>28.5 ± 1.0</td>
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</tr>
<tr>
<td>WM 40 (Control)</td>
<td>829.7 ± 23.3</td>
<td>200.9 ± 6.6</td>
<td>20.28 ± 0.44</td>
<td>375.4 ± 7.9</td>
</tr>
<tr>
<td>WM 40 (200 kGys)</td>
<td>970.2 ± 27.1</td>
<td>259.2 ± 10.9</td>
<td>25.26 ± 0.82</td>
<td>435.7 ± 10.8</td>
</tr>
<tr>
<td>WM 50 (Control)</td>
<td>759.2 ± 49.7</td>
<td>207.9 ± 19.8</td>
<td>14.91 ± 0.4</td>
<td>246.0 ± 15.9</td>
</tr>
<tr>
<td>WM 50 (80 kGys)</td>
<td>942.2 ± 20.3</td>
<td>260.0 ± 25.7</td>
<td>17.59 ± 1.04</td>
<td>348.3 ± 13.3</td>
</tr>
<tr>
<td>WM 50 (200 kGys)</td>
<td>986.6 ± 18.8</td>
<td>258.4 ± 17.6</td>
<td>20.84 ± 1.5</td>
<td>363.5 ± 19.6</td>
</tr>
<tr>
<td>WM 60 (Control)</td>
<td>1065 ± 29.0</td>
<td>244.9 ± 15.7</td>
<td>12.77 ± 0.65</td>
<td>268.85</td>
</tr>
<tr>
<td>WM 60 (200 kGys)</td>
<td>944.0 ± 22.7</td>
<td>156.5 ± 10.1</td>
<td>7.17 ± 0.45</td>
<td>47.2 ± 6.4</td>
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</table>

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A2.1 Introduction

Among the many issues that must be considered for environmentally degradable thermoplastic applications of starch, an important one is the effect, at the molecular level, of different kinds of processing on starch polymers. The obvious and most direct way to study this is through a careful molecular characterization of the starch before and after processing. Unfortunately, this sounds more straightforward than it actually is; starch molecules are notorious for presenting the investigator with a plethora of problems that serve as obstacles to simple application of the traditional methods of polymer molecular characterization. Some of the problems are summarized here.

Almost all techniques for probing the molecular size and structure of polymers are based on measurements of their dilute solution properties, where the interactions between individual molecules are eliminated (or at least minimized). However, in the case of starch, just the first step, i.e., obtaining molecularly dispersed solutions, can be quite a complicated task. Starch molecules display strong inter-molecular forces in their native solid state; initial dissolution necessitates disruption of these forces. This often requires dissolution at elevated temperatures, whereby degradation also becomes an important consideration. Furthermore, the amylose molecules present in the starch granules tend to go into solution in preference to the amylopectin molecules; therefore care must be taken to ensure that the complete sample goes into solution. Once in solution, amylose molecules have a tendency to crystallize and drop out of solution ("retrograde"), while the amylopectin is relatively stable in solution. In alkaline solution, the ether linkages in starches are susceptible to attack from the oxygen dissolved in the solvent during ambient
exposure; this requires dissolution in oxygen-free solvent, and limiting the ingress of oxygen once the sample is in solution. Although some aspects of these characteristic tendencies of starch molecules have been of some use as the basis of various fractionation and purification procedures, they can be barriers to obtaining solutions suitable for molecular analyses. Care must be taken to keep these potential problems in mind, while preparing solutions of starch samples for analysis. Generally, alkaline solutions (with normality ranging from 0.1 to 1) at room temperatures and dimethyl sulfoxide at elevated temperatures have enjoyed the greatest popularity as solvents for dilute solution analyses of starch and its components.

Most starches occur as mixtures of amylose and amylopectin molecules. The fraction of each component, and the molecular size and structure of each depends upon the source of the starch; even within one sample, there can be large distribution of molecules of various sizes and shapes. Quantitative assessment of the molecular weight changes from intrinsic viscosity measurements on polymer samples is based on estimation of their viscosity-average molecular weights ($\bar{M}_v$) using the Mark-Houwink relationship, $[\eta] = K' \bar{M}_v^a$. Unfortunately, for starches, such a calculation is possible only for the linear amylose components, since the Mark-Houwink parameters ($K'$ and $a$) for whole starches and amylopectin are generally not available. Where estimates for these parameters are available, their general applicability could be questionable since they will very likely be dependent upon the structure of the branched components (as for dextran, for example (Senti et al. 1955)). The structure of these components, in turn, may vary with the processing the starch undergoes. In fact, the procedure for fractionating starch into its components for detailed intrinsic viscosity measurements could itself effect macromolecular modifications. This could be partly responsible for measurements reported in literature where the average intrinsic viscosities of the whole starch samples are significantly
different from the weighted intrinsic viscosities of the fractionated amylose and
amylopectin components (Colonna et al. 1984), in contrast to the usual weighted additivity
of the components' intrinsic viscosities for macromolecular mixtures (Weaver et al. 1988).
Therefore, bulk intrinsic viscosity measurements are not of much use in estimating absolute
molecular weights of starch samples; however, changes in the solution properties of the
same sample before and after processing can serve to provide some qualitative assessment
of the molecular changes induced by the process.

Gel permeation chromatography, the most common technique for determining
molecular weight distributions of polymers, allows the fractionation of molecules
according to their molecular size (the sequence of elution depends on hydrodynamic
volume, not absolute mass). The hydrodynamic volume scales as the product of intrinsic
viscosity, [η], and the molecular weight of the molecule, M, for random-coiling linear and
homogeneous branched polymers (Grubisic et al. 1967). This leads to the universal
calibration curve based on narrow molecular weight distribution polymers. The MWDs of
different polymer samples may then be calculated if the Mark-Houwink parameters relating
[η] to M are known. However, there are three situations where such an analysis is not
applicable: (a) if the sample does not follow the universal calibration (Dubin and Principi
1989), (b) if intrinsic viscosity (Mark-Houwink) parameters of the polymer to be analyzed
are unknown, or (c) if there is a mixture of molecules of different chemical or physical
structure within the same elution slice. For materials such as unfractionated starches which
contain a mixture of linear and branched macromolecules (and where the branching
architecture might vary with the molecular weight), determination of the effective Mark-
Houwink parameter for any elution slice in a chromatographic experiment becomes an
extremely difficult proposition. In such cases, the traditional GPC experiment yields
mainly qualitative information about changes in the MWDs of the starch samples.
Fractionation of starch into its components would still allow the universal calibration to be applied only for the amylose (again due to availability of Mark-Houwink coefficients only for amylose). For such complex polymer systems, multi-detection gel permeation chromatography is of particular use by allowing the elucidation of the absolute molecular weight of each elution slice directly, and hence the absolute molecular weight distribution of the polymer. Such systems are based on concentration sensitive detectors (such as differential refractive index (DRI)) coupled with light scattering (LS) and/or differential viscometric (DV) detectors. In recent years, the use of multiple detectors for gel permeation chromatography (GPC) has become more common. The majority of our analyses involved utilization of a GPC system with DRI and LS detectors to get a direct determination of the molecular weight distributions of various starch samples.

A2.2 Estimation of Inter-Detector Lag in Multi-Detection Gel Permeation Chromatography

Accurate determination of absolute molecular weights using multi-detection gel permeation chromatography requires a precise estimation of the inter-detector lag such that the concentration and LS or DV signals corresponding to any elution slice are correlated correctly. Several methods for estimating this lag have been reported in the literature (Lecacheux and Lesec 1982, Mourey and Miller 1990, Billiani et al. 1990, Balke et al. 1990, Kuo et al. 1987) that are based on a variety of experimental techniques or analyses. Presented here is a different method for estimating the detector lag between a concentration detector and a second detector in which the signal is dependent on the molecular weight of a polymer sample. This straightforward method is analytical in its approach and does not require any knowledge about the MWD of the polymer sample used in the analysis.
A2.2.1 Theory

In GPC, the elution volume of a polymer molecule depends on its hydrodynamic size, not its mass. In most cases, the sample injected in GPC contains molecules of the same class, e.g., linear, star, comb, so that the sizes of molecular species increase as the molecular weights increase. Thus, in general, increasing elution volumes correlate with decreasing molecular weights (exceptions being non-homogeneous samples, such as those containing mixtures of both linear and branched polymer molecules). In a multi-detection GPC run, one signal (e.g., DRI) depends only upon the concentration of the solute molecules, while the molecular weight dependent signal (LS or DV) is a function of both the concentrations as well as the molecular weights of these eluting molecules. Therefore with increasing elution volumes, the molecular weight dependent signal will generally peak before the concentration signal because of the constantly decreasing contribution from the molecular weights of the eluting solute molecules. Consequently, the peaks corresponding to these two signals would be offset even if the two detectors were at the same position in the flow system. In reality, different detectors are at different positions in the flow system which leads to a lag between their signals.

A2.2.1.1 Light Scattering Detector

If we consider the case of the LS detector, we have the signal measured from any elution slice as being proportional to the excess Rayleigh ratio, $R_\theta$

$$R_\theta = K c [M P(\theta) - 2 A_2 c M^2 P^2(\theta)]$$  \hspace{1cm} (1)

where $c$ is the concentration of the polymer of molecular weight $M$ in that elution slice, and $A_2$ is the corresponding second virial coefficient. $P(\theta) = 1 - 2 \mu^2 <r_g^2> / 3! + \ldots$ is commonly termed as the structure factor (where $\mu = (4 \pi / \lambda) \sin (\theta / 2)$, $\lambda$ being the wavelength of the incident light, and $r_g$ the radius of gyration) and $K$ is an optical constant.
In a GPC experiment, realistic upper estimates for the concentration are approximately $10^{-4} - 10^{-5}$ g/cc at the peak of the concentration chromatogram, and generally $A_2 = 10^{-3} - 10^{-4}$ mol cc/g. As a result, the $A_2$ term in Eq. 1 can usually be neglected for GPC-LS calculations. Therefore, for our purposes, Eq. 1 can be written as:

$$R_\theta = KcMP(\theta)$$  \hspace{1cm} (1a)

(although this simplification does not have an effect on the final outcome of our analysis).

For further simplifying the analysis, we would like to set $P(\theta) = 1$. If $P(\theta) \neq 1$, then the analysis becomes slightly more complex since $P(\theta)$ is a function of $r_g$ and $r_g$ in turn, varies with the elution volume. For a low-angle laser light scattering (LALLS) detector, since $\theta$ is small, $P(\theta) = 1$ in any case. For a MALLS detector, $P(\theta) \neq 1$ for higher angle detectors unless $r_g << \lambda$ (i.e., the scattering molecules are small). However, it is preferable, if possible, to use LS signals from a higher angle detector (such as 90°, for example) since they are less susceptible to noise due to extraneous scatterers. Therefore, when this analysis is applied to MALLS detectors, the preferred strategy is to use higher angle LS signals from scatterers small enough such that $P(\theta) = 1$.

With the assumption of $P(\theta) = 1$, the dependence of the LS signal on the elution volume, $v$, can be written as:

$$\frac{dR_\theta}{dv} = \frac{\partial R_\theta}{\partial c} \frac{dc}{dv} + \frac{\partial R_\theta}{\partial M} \frac{dM}{dv}$$  \hspace{1cm} (2)

From Eq. (1), we obtain

$$\frac{\partial R_\theta}{\partial c} = KM$$  \hspace{1cm} (3a)

and

$$\frac{\partial R_\theta}{\partial M} = Kc$$  \hspace{1cm} (3b)
The elution dependence of polymer molecules from GPC columns can generally be written as an equation of the general form:

\[ \log M = B - D v \quad (4) \]

\[ \Rightarrow \frac{dM}{dv} = -2.303D10^B \cdot Dv = -2.303DM \quad (5) \]

The concentration peak occurs at \( \frac{dc}{dv} = 0 \), while the LS peak occurs at \( \frac{dR_\theta}{dv} = 0 \).

From Eq. (2), we see that for \( \frac{dR_\theta}{dv} = 0 \),

\[ \frac{\partial R_\theta}{\partial c} \frac{dc}{dv} = -\frac{\partial R_\theta}{\partial M} \frac{dM}{dv} \]

\[ \Rightarrow KM \frac{dc}{dv} = -Kc \frac{dM}{dv} \quad (6) \]

Using Eq. (5), we rewrite the above condition as:

\[ \left[ \frac{dc}{dv} \right] \frac{dR_\theta}{dv} = 0 = 2.303 Dc \quad (7) \]

Since all quantities on the right hand side of Eq. 7 are finite (even though small), we can conclude that under practical GPC conditions, \( \frac{dc}{dv} \neq 0 \) when \( \frac{dR_\theta}{dv} = 0 \) (unless the sample is perfectly monodisperse). Thus the peaks of the concentration and the LS chromatograms generally cannot be matched to get the detector lag since they both do not represent the same elution slice.

Given all this, in order to find the inter-detector lag, we need to find the elution slice on the concentration chromatogram that should correspond to a known slice on the LS chromatogram. We choose, as our reference slice, the peak of the LS signal. Referring to Eq. 7, we see that the elution slice corresponding to \( \frac{dR_\theta}{dv} = 0 \) is the slice on the concentration curve (at elution volume \( v^* \)) where

\[ \frac{1}{c} \frac{dc}{dv} = 2.303D. \quad (7a) \]
The quantity on the left hand side is easily evaluated by fitting the peak portion of the concentration chromatogram with a smooth curve, and then calculating the fractional slope as a function of elution volume. The offset between the peaks of the concentration and the LS signals is given by $v_{\text{peak concentration}} - v^*$. The inter-detector lag then is the difference between the $v_{\text{peak LS}}$ and $v^*$ for the data as it is received by the collection instrument (since $v_{\text{peak LS}}$ and $v^*$ would coincide if there was no lag).

Once the concentration and LS chromatograms have been obtained for the sample being utilized in the lag estimation procedure, a value for $D$ (the slope of the log molecular weight vs. elution volume curve for this polymer-column combination) is required. It is possible to determine the true value of $D$ independently from a traditional GPC calibration procedure, such as the peak calibration method (Yau et al. 1979); this true value of $D$ should directly yield, in one step, the correct detector lag using Eq. 7a. However, the availability of the true value of $D$ is not a requirement; some reasonable estimate of $D$ can be used as an initial value in an iterative procedure. The first calculation yields a first estimate of the detector lag. At this point, the GPC-LS calculations should be carried out for the sample with this value of detector lag. These calculations will yield an estimated molecular weight vs. elution volume plot for this sample. The slope of this plot should be entered as the next estimate for $D$ in a new iteration of the above procedure to yield another detector lag value and hence another apparent molecular weight vs. elution volume plot. These iterations should be carried out until the detector lag converges to a constant value. With this value, the slope of the molecular weight vs. elution volume plot is the true $D$ for this polymer-column combination. The final convergence value does not depend on the initial estimate of $D$. It should be noted here that this iterative procedure is more cumbersome given the necessity of careful evaluations of $D$ from the sample data.
A2.2.1.2 Differential Viscometry Detector

In a viscometric detector, the signal being measured is the pressure drop of the fluid as it flows through a capillary tube. This pressure drop is proportional to the viscosity of the fluid. For polymer solutions, the intrinsic viscosity, \([\eta]\), is evaluated by the equation:

\[
\ln \left( \frac{\eta_s}{\eta_0} \right) = \frac{1}{c} [\eta] + k'' [\eta]^2 c
\]

where the subscript "o" refers to the solvent, and "s" refers to solution containing the polymer at concentration \(c\). \(k''\) is referred to as the Kraemer constant. For low concentrations (typical in GPC experiments), \(k'' [\eta] c \ll [\eta]\). Therefore, the pressure drop measurement, \(p\), of any elution slice allows the evaluation of the intrinsic viscosity of that slice through the relationship:

\[
[\eta] = \frac{1}{c} \ln \left( \frac{P}{P_0} \right).
\]

This intrinsic viscosity is dependent upon the polymer molecular weight as \([\eta] = K' M^\alpha\), where \(K'\) and \(\alpha\) are the Mark-Houwink constants for a polymer. Substituting for \([\eta]\) from the Mark-Houwink equation and rearranging:

\[
\ln \frac{P}{P_0} = c K' M^\alpha
\]

Differentiating, we get

\[
\frac{d (\ln \frac{P}{P_0})}{dv} = K' c \frac{d(M^\alpha)}{dv} + K' M^\alpha \frac{dc}{dv}
\]

Substituting from Eq (4) and setting \(\frac{d (\ln \frac{P}{P_0})}{dv} = 0\),

\[
K' M^\alpha \frac{dc}{dv} = - K' c \frac{d(10^{\alpha(B - D \nu)})}{dv}
\]

\[
= 2.303 D \alpha K' c (10^{\alpha(B - D \nu)})
\]
Thus the elution slice on the concentration curve corresponding to \( \frac{d \left( \ln \frac{P_v}{P_0} \right)}{dv} = 0 \) is given by:

\[
\frac{1}{c} \frac{dc}{dv} = 2.303 D \alpha \tag{13}
\]

The detector lag can then be evaluated in a method similar to that mentioned in part A. However, in this analysis, the constant \( \alpha \) needs to be pre-determined in order to carry out the calculations. One could either use a polymer sample for which \( \alpha \) is available in the literature, or use narrow standards of the polymer to determine \( \alpha \) from intrinsic viscosity experiments.

A2.2.2 Experimental

The experiments were carried out on the DAWN-F (Wyatt Technologies, Santa Barbara, CA, USA) MALLS detector (\( \lambda = 6328 \text{ Å} \)) coupled to a 150-C (Waters, Milford, MA, USA) GPC system. The chromatography was carried out using a combination of Waters Ultrahydrogel 500 and 2000 columns, with a guard column, at 25 °C. The mobile phase was water (containing 0.02% NaN₃ as a bacteriostat) with a flow rate of 0.92 ml/min. The analyses were performed using Lotus 1-2-3 (Lotus, Cambridge, MA, USA) and the Astra program provided with the DAWN-F. Curve fitting was carried out with Microsoft Excel (Microsoft, Redmond, WA, USA). Polymers utilized in the studies were narrow MWD polyethylene oxide (PEO) standards, molecular weights ranging approximately from 50,000 to 900,000 (Toyo Soda, Japan), and a broad MWD PEO sample, nominal molecular weight 200,000 (Polysciences, Warrington, PA, USA).
A2.2.3 Results and Discussion

The detector lag estimation analyses were carried out on the DRI signals from narrow MWD PEO samples of molecular weight less than 100,000. The $v_{\text{peak LS}}$ for each sample was evaluated from the 90° LS detector signal. The resulting mean value of the detector lag was then used in subsequent molecular weight calculations with the GPC-LS data. The analyses on the low molecular weight polymer samples yielded an estimated detector lag of $0.124 \pm 0.009$ ml. The elution behavior of a number of different PEO samples was then obtained using the mean value of the detector lag in the molecular weight calculations. The elution behavior, thus obtained, for the broad and narrow MWD PEO samples overlapped, as they should. Figure A2.1 shows the data for the elution dependence of the broad MWD sample.

As pointed out in the literature (Moorey and Miller 1990), the slope of the elution curve is sensitive to the inter-detector lag. Too high a value of detector lag leads to an artificially flat elution curve, while too low a value leads to too steep a curve. (This is especially noticeable for narrow MWD samples, since changing the value of the detector lag leads to significant changes in the polymer concentration assigned to any elution slice. Calculations for broad MWD samples are generally less susceptible to this problem since their concentration chromatograms are spread out.) Therefore, we can use the slope of the elution curve as the parameter to ascertain the accuracy of our method. For this purpose, the absolute reference elution curve was obtained from a traditional GPC peak calibration method using only the DRI detector with narrow MWD standards (of the same polymer as the samples used for the analysis). Shown in Figure 1 is the elution dependence (linear over the evaluation range) corresponding to such a GPC peak calibration method using the narrow MWD PEO standards was Examination of Figure 1 shows that the elution curve obtained by using the estimated detector lag correlates well with the peak calibration data.
Since the detector lag obtained by our analysis yields (from the GPC-LS data) an elution curve for a polymer-column combination that agrees with the reference curve, the value of the lag must be correct.

The methods described by Balke et al. (1991) and Kuo et al. (1987) determine the inter-detector lag (for GPC-LS and GPC-DV systems, respectively) by comparison with reference data obtained from calibration with narrow MWD standards. In a sense, the philosophical underpinnings of our one-step method (i.e. utilizing the slope from a reference curve directly for the calculation of the inter-detector lag) are similar to these methods, the major difference being that they obtain the inter-detector lag through an empirical approach, while we use an analytical one. On the other hand, our iterative method, though not as simple, obviates the necessity of the reference data for obtaining the inter-detector lag.

Some points should be noted here:

1. It is easier to carry out the lag estimation with reasonably narrow MWD samples since they provide high \( \frac{dc}{dv} \) values. However, broad distribution samples are also utilizable, as long as the peak slices can be easily identified. If the iterative procedure is being followed, the intermediate estimates of D (from the sample data) must be evaluated carefully since the data range is small.

2. The calculation for the offset of the two peaks are carried out on the concentration curve. Generally concentration detectors have a less noisy signal than molecular weight sensitive detectors since the former are not affected by very small concentrations of large contaminants (mainly dust). Still, the calculations of the fractional slope must be accurate, since the accuracy of the method depends on this quantity directly.
3. If we use the D value from a previous iteration in the next iteration of the analysis, the effects of column dispersion do not bias our values. This is consistent with the fact that one cannot expect the detector lag to be a function of the column efficiency.

4. Since the method described here utilizes GPC columns in-line, both the concentration and molecular weight dependent signals have lower noise by virtue of the columns eliminating most extraneous scatterers in the flow field (particularly important for aqueous systems) as well as suppressing the pressure fluctuations due to the pump.

5. This analysis assumes the elution curve to be linear over the elution volume range under consideration. Generally, this should hold, especially for narrow MWD samples, but if this linearity condition does not hold, the analysis would need to be modified if it is to be utilized.

### A2.3 Starch Fragmentation During Extrusion Processing

Extrusion processing of starch has been traditionally used in the food industry, a number of studies have dealt with estimating the nature and extent of extrusion-based molecular modification of starches (Gomez and Aguilera 1983, Jackson et al. 1990, Colonna and Mercier 1983, Davidson et al. 1984, Colonna et al. 1984, Diosady et al. 1987, Wen et al. 1990, Rodis et al. 1993). These studies indicate that under the high-shear, high-temperature conditions that exist during such processing, starches can undergo a variety of changes at the intra- and inter-molecular level. One important effect, that of the fragmentation of starch, leads not only to changes in its molecular weight and the molecular weight distribution (MWD), but also in the structure of the molecules, which is not surprising given the nature of starch (generally a mixture of amylose (linear or long-chain branched molecules) and amylopectin (highly branched molecules)). Since the physical and mechanical properties of polymeric materials are a function of such molecular
parameters, a study of this fragmentation phenomenon is of particular interest for thermoplastic applications of starch where some required levels of mechanical performance are likely to be required.

In the past, conclusions of starch fragmentation during extrusion processing have been based on bulk measurements such as water solubility (Gomez and Aguilera 1984, Jackson et al. 1990, Colonna and Mercier 1983, Davidson et al. 1984), intrinsic viscosity (Colonna and Mercier 1984, Davidson et al. 1984, Colonna et al. 1984, Diosady et al. 1987), light scattering (Colonna et al. 1984), as well as on size-fractionation-based measurements, namely gel permeation chromatography (GPC) (Jackson et al. 1990, Colonna and Mercier 1983, Davidson et al. 1984, Colonna et al. 1984, Wen et al. 1990, Rodis et al. 1993), with the last category yielding mainly qualitative information for reasons discussed later. This study involves an investigation of extrusion-processing-induced starch fragmentation utilizing gel permeation chromatography-light scattering.

A2.3.1 Experimental

The basic material for this study was an acid-modified high-amyllose starch (National Starch EK Fl. Hylon 7, approximate amyllose content 70%). This material was conditioned at 50% relative humidity, and then processed in a twin screw, co-rotating extruder (Leistritz Standard Model 34), as indicated in Chapter 2. Glycerine and some additional water were added to the feed to act as plasticizers. Overall, the glycerine and water contents of the material in the extruder were 13.7% and 17.7% of the total feed by mass, respectively. A small amount of low molecular weight processing aids were also added (<1% of the total feed by mass). The peak temperature in the extruder was 170 °C, and a screw speed of 150 rpm was used during the processing, resulting in a die pressure between 55 and 88 MPa (George et al. 1994). Pellets from the extruded material were
powdered, and used in the characterization studies. This material is hereafter referred to as the extruded starch.

The chromatography was carried out as described in Chapter 2, except that the low rate was 0.19 ml/min. Also, the value of the inter-detector lag used was the one obtained in section A2.2 since these experiments were carried out soon after switching the chromatographic system to the alkaline mobile phase. Intrinsic viscosity of the starch samples was measured using a Ubbelohde viscometer in a water bath maintained at 25 °C, with aqueous 0.5N NaOH as the solvent. The starch solutions for the chromatography as well the intrinsic viscosity experiments were prepared by dissolving the samples in degassed 0.5N NaOH and filtered with a Millipore LCR 0.5 μm filter prior to use in measurements.

Starch concentrations of the solutions used in the intrinsic viscosity measurements were obtained by the phenol-sulfuric acid colorimetric method (Dubois et al. 1956). This involved adding concentrated sulfuric acid (reagent grade, 96%) to a small quantity of starch (5 ml. acid to approximately 125 μg of starch) to reduce the starch to the glucose units. 125 μl of 80% phenol solution was then added to this mixture, and the absorbance of the resulting complex measured at 488 nm. The absorbance was converted to starch content using a calibration curve constructed previously with a purified amylose standard.

A2.3.2 Results and Discussion

Figures A2.2a and A2.2b show the DRI and LS signals obtained from the GPC experiment for the unextruded and extruded high-amylose starch. For both the samples, the elution profile obtained from the DRI detector indicates molecules in significant concentrations over a large range of hydrodynamic sizes (the theoretical exclusion limit for this column set is estimated by the manufacturer to be poly(ethylene oxide) of molecular
weight of $10^7$). The first peak is the amyllopectin component of the starch, eluting early due to its very large size. Partially overlapping with this is the second, broad peak attributable to the amyllose component. A large peak (from the processing aids and other low molecular weight extraneous material) was also present at the permeation volume of the columns.

The LS signal, on the other hand, is very different from the DRI trace due to the fact that it is proportional to the product of the concentration and the molecular weight of the polymer molecules in any elution slice. The initial sharp rise of this signal to a high value indicates some moieties of extremely high molecular weight were excluded from the pores of the packing in the chromatographic columns. The signal intensity drops quite quickly, however, due to the decreasing scattering contribution from the (lower molecular weight) materials at higher elution volumes.

Concentration (elution) profiles reported in literature (Colonna and Mercier 1983, Colonna et al. 1984, Wen et al. 1990, Rodis et al. 1993) indicate that the initial peak (attributable to amyllopectin) shows significant reductions for extrusion-processed samples. Comparing the two samples in our case, the amyllopectin peak shapes are not very different, and the amyllose peak flattens out to some extent. The difference between our observations and those in literature are probably due to the fact that our starting material is different from that used by the others, in that it is acid-modified previous to the thermo-mechanical processing. Acid attack upon starch occurs preferentially in the amorphous region of the granule (Rohwer and Klem 1984), with cleavage of some or all of the macromolecules (French 1984). Amylopectin molecules in corn starch might be initially cleaved to a greater extent than the amyllose molecules during acid-modification (Rohwer and Klem 1984). Therefore, it is possible that the amyllopectin molecules in the unprocessed starch used in this study had already been fragmented to some extent, and as a
consequence, did not undergo the same level of degradation upon extrusion processing (relative to the unextruded material) as observed by others. It should also be noted that although the processing was carried out at a relatively high temperature, the total plasticizer fraction in the extruder was around 30%, with a part of the plasticizer being glycerin. It is not known whether glycerin and water might act differently in shielding the starch from shear forces during the extrusion processing.

Figure A2.3 presents the molecular weights for the two starch samples, (i.e., before and after the extrusion processing) as a function of the elution volume, calculated from their DRI and LS signals. The molecular weight calculations were carried out only for elution volumes less than 17 mls. At higher elution volumes, the LS signal is quite low; given the unavoidable noise from the dust and other extraneous scatterers in the aqueous mobile phase, the LS signal-to-noise ratio is too low in this regime for meaningful calculations. This is illustrated by the increased scatter in the molecular weight values for the extruded starch sample as the elution volume approaches 17 mls. As a result, it was not possible to obtain average molecular weights for the whole sample with this GPC-LS experiment. However, the elution volume range over which the molecular weight calculations were carried out contains the fraction of the molecules that should provide the dominant contribution to the weight-average molecular weight of the whole sample (since this high molecular weight fraction accounts for the majority of the LS signal). With this in mind, we can roughly estimate the overall weight-average molecular weights for the starch samples before and after extrusion-processing to be $3.2 \times 10^6$ and $2.4 \times 10^6$, respectively.

The molecular weight vs. elution volume data indicates that at any given elution volume, the extrusion-processed starch displays a lower molecular weight (or conversely, for a given molecular weight, the unextruded starch molecules have a higher elution volume (and therefore, a smaller hydrodynamic size) than their processed counterparts).
Since the two polymer samples are chemically identical, a difference in the molecular weight for the same elution volume can only be due to some differences in the architecture of the molecules (in the two samples) that elute at the same time. Amylopectin molecules are highly branched, and the amylose in high-amylose maize starches is known to have long-chain branching. In the literature, dilute solution studies on branched macromolecules such as star polymers indicate that such molecules are more compact (and increasingly so with increasing functionality) than their linear counterparts of equivalent molecular weight (Bauer et al. 1989, Roovers et al. 1993). Other work on chemically-modified starches has shown that for fractions of equal molecular weight, an increased degree of branching corresponds to a higher hydrodynamic density (Sommermeyer et al. 1992). In our study, the observed reduction in the molecular weights at a given elution volume for the extrusion-processed starch (relative to the unextruded starch) could be similarly due to some debranching of the branched macromolecular components of the starch during the thermo-mechanical processing treatment. Debranching as a mechanism for fragmentation during extrusion processing has been previously reported in literature, although the conclusions were based on observations in reductions in peak size for the amylopectin fraction during GPC of starch (Davidson et al. 1984). This current study indicates that the amylose also loses branches during the extrusion processing, not surprising given the fact that the (almost) linear amylose molecules are likely to be significantly influenced by the high shear in the extruder.

The intrinsic viscosity of the unprocessed and processed samples were measured to be 108 ml/g and 95 ml/g respectively. This is only a modest reduction, but in any case intrinsic viscosity is not a very sensitive measure of the molecular properties of branched molecules. The reduction in intrinsic viscosity is consistent with the GPC-LS data indicating that the extrusion-processing of starch leads to fragmentation of the molecules.
Fig. A2.1. Data showing elution behavior of broad MWD PEO samples using GPC-LS with the detector lag value obtained by this method (rough line) and elution curve for traditional peak calibration method using narrow MWD PEO samples (smooth line). The reference elution curve is extrapolated for clarity (dashed line).
Fig. A2.2: LS and DRI detector signals for high-amylose starch: (a) Control sample
Fig. A2.2: (b) Extrusion-processed sample

Detector Signal
Fig. A2.3: Molecular weight as a function of elution volume for the control (Δ), and extrusion-processed (+) high-amylose starch
References


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