

**<sup>60</sup>Co Radiation Effect on Copolymers of Starch and Plastics<sup>1</sup>**ANANTHA N. R. KOLLENGODE,<sup>2</sup> SANDEEP BHATNAGAR,<sup>3</sup> and MILFORD A. HANNA<sup>4</sup>**ABSTRACT**

Cereal Chem. 73(5):539–542

Normal corn starch (25% amylose content) was mixed with 10% of either polystyrene or poly(methyl methacrylate) and irradiated at 0, 5, 10, 20, or 30 kGy. The irradiated samples were extruded using a C. W. Brabender twin-screw laboratory extruder at 120°C barrel temperature, 60 rpm screw speed, and 18% (db) moisture content. Level of radiation

significantly ( $P > F = 0.001$ ) influenced extrudate radial expansion ratio, bulk density, specific mechanical energy, water solubility index, and degree of grafting as determined by  $\delta^{13}\text{C}$  values. These properties were not significantly influenced by the type of plastic polymer used.

The low cost of corn starch, coupled with its abundant availability, has made it an attractive candidate for use in development of biodegradable starch-plastic composites (Swanson et al 1993). A number of researchers have worked on development of starch-based plastics (Fanta et al 1979; Maher 1979; Rayford et al 1979; Fanta et al 1980; Chinnaswamy and Hanna 1991; Bhatnagar and Hanna 1995a,b) with the goal of preparing disposable packaging materials with the least amount of synthetic polymer in their formulations. These degradable polymers are used as alternatives for nondegradable polymeric film products made from polyethylene or polypropylene and foam products made from polystyrene. Degradation into environmentally friendly substances after disposal is due to a combination of photodegradation, chemodegradation (water and oxygen), biodegradation (microorganisms and enzymes), and mechanical degradation (wind) (Roper and Koch 1990).

Of the methods employed, graft polymerization using extrusion has been successful for starch-thermoplastic polymer composite manufacturing (Swanson et al 1993). Graft polymerization results in chemical bonding rather than physical mixing of starch and synthetic polymer, which in turn results in a more intimate association of the two dissimilar polymers (Patil and Fanta 1993).

The synthesis of starch graft copolymers is achieved primarily by free radical initiation (Fanta et al 1980). Free radical initiators such as ceric ammonium nitrate (Fanta 1973, Rayford et al 1979, Fanta et al 1980); redox systems (Maher 1979; Rayford et al 1979; Hebeish et al 1988a,b), and high energy radiation (Fanta et al 1979, Fanta et al 1980, Trimell and Stout 1980) are commonly used to cross-link starch to synthetic monomers.

$\gamma$ -Radiation has been reported to cause number of chemical and molecular changes in carbohydrates, resulting in numerous radiolytic products (Adam 1983). Grant and D'Appolonia (1991) observed formation of new branching and possible relocation of branch points in polysaccharides such as starch, even during low levels of irradiation.

While extensive research has been done using chemical free radical initiators and vinylic or acrylic monomers (Hebeish et al 1988a, Chinnaswamy and Hanna 1991, Carr et al 1992, Yoon et al

1993), the effect of irradiating plastic polymers and starches on the physical properties of resultant extrudates has not been reported. The present research was an attempt to prepare starch plastic grafts from polystyrene (PS) or poly(methyl methacrylate) (PMA). The latter one was selected because it is considered more environmentally friendly as compared to polystyrene (Bhatnagar and Hanna 1995a,b).

**MATERIALS AND METHODS****Materials**

Normal corn starch was contributed by American Maize Products Co., Hammond, IN. Powdered starch was agglomerated by steadily spraying distilled water onto the starch in an inclined and rotating pan and drying to 9–12% moisture content at room temperature. PS and PMA were obtained from Dow Chemicals, Midland, MI, and Polymer Sciences, Warrington, PA, respectively. Ingredient specifications are listed in Tables I and II.

**Extrusion**

Starch extrusions were performed in a twin-screw laboratory extruder (model 2803, Plasticorder, C. W. Brabender Instruments, Inc., South Hackensack, NJ) with a 1.9-cm barrel diameter, a 20:1 barrel length to diameter ratio, and a 7-mm cylindrical die nozzle. Barrel temperatures of feed, compression, metering, and die sections were maintained at 60, 120, 120, and 120°C, respectively. Screw speed was maintained at 60 rpm. The details of screw configuration are reported in Sokhey et al (1994). Extrusion was replicated twice for each treatment.

 **$\gamma$ -Radiation**

Starch samples were mixed with 10% by weight of either PS or PMA and treated with 0, 5, 10, 20, or 30 kGy of  $\gamma$ -radiation, at room temperature, using the <sup>60</sup>Co irradiator maintained by the Radiation Safety Office of the Department of Environment Protection at University of Nebraska, Lincoln. The dosage rate was standardized by Landuer, Inc., Glenwood, CO, at 0.54879 kGy/hr. The times of exposure required to generate the respective radiation levels were (hr:min): 0:00, 9:07, 18:13, 36:27, and 54:40.

**Radial Expansion Ratio**

Radial expansion ratio was calculated by dividing the cross-sectional area of extrudate by the cross-sectional area of the die nozzle (Sokhey et al 1994). Each value was a mean of 10 observations.

**Bulk Density**

Bulk densities of the extrudates were calculated as:  $\rho = 4W/(\pi \times D^2 \times L)$  where  $W$  = weight of extrudate (kg),  $\rho$  = bulk density

<sup>1</sup>Published as Journal Series No. 11406 of the University of Nebraska Agricultural Research Division.

<sup>2</sup>Graduate research assistant, Industrial Agricultural Products Center, University of Nebraska, Lincoln, NE.

<sup>3</sup>Research associate, Industrial Agricultural Products Center and Department of Biological Systems Engineering, University of Nebraska, Lincoln, NE.

<sup>4</sup>Professor, Departments of Food Science and Technology and Biological Systems Engineering, and Director, Industrial Agricultural Products Center, Univ. of Nebraska, Lincoln, NE 68583-0730. Corresponding author. E-mail: bsen024@unlvm.unl.edu

(kg/m<sup>3</sup>),  $D$  = average diameter of the extrudate (m), and  $L$  = length (m) of 1 kg of extrudate (Bhatnagar and Hanna 1994).

### Specific Mechanical Energy

Specific mechanical energy (SME) was determined using the method described by Sokhey et al (1994). The net mechanical energy input to the screws was divided by the extrudate flow rate (dry basis). The net mechanical energy input to the extruder was calculated from torque and angular velocity measurements. The torque input to the extruder was recorded by a computer interface and controller unit (PL2000 controller, C. W. Brabender) using a software Program loader version 1.9.5 (Brabender [R] OHG).

### Water Solubility Index

Water solubility index (WSI) was the amount of solids recovered by evaporating the supernatant obtained from 1 g of sample and was expressed as percent of dry solids of the extrudates. WSI was determined by the method of Bhatnagar and Hanna (1994). Ground extrudates ( $\approx 0.5$  g) were dissolved in 30 ml of water in centrifuge tubes. The dissolved samples were stored for 30 min with periodic stirring and then centrifuged at  $5,000 \times g$  for 10 min. The supernatants were carefully decanted into petri dishes and solute concentrations were determined by oven-dry method.

### Determination of Degree of Grafting

A sequential extraction procedure was used to separate starch-polymer grafts. Extrudates were ground in a Tecator micromill (Tecator, Inc., Silver Spring, MD) to pass through a 50-mesh screen. They were then extracted with water to remove small molecular weight carbohydrates (unreacted) or small plastic grafts. The residues were then extracted with chloroform to remove pure PS or PMS and small starch grafts (Chinnaswamy and Hanna 1991). The remainder was considered to be starch-polymer grafts. The samples of starch, synthetic polymers, and isolated starch grafts were combusted at high temperatures, and CO<sub>2</sub> compositions were analyzed precisely in an isotope ratio mass spectrophotometer (Delta-S, Fannigan, Germany) coupled with Hercus elemental analysis as described by Chinnaswamy and Hanna (1991).

### Statistical Analysis

Data were analyzed using a statistical computer package (Vers. 6.0, SAS Institute, Cary, NC). The experimental design was a randomized complete block design with blocking over replicates and type of synthetic polymer, and three replicates for each treatment.

TABLE I  
Proximate Analyses of Corn Starch<sup>a</sup>

Total amylose (% dwb)	25.0
Protein (% dwb)	0.3
Phosphorus (mg/100 g)	14.2
Lipid (g/100 g)	0.1
Ash (g/100 g)	0.2
Moisture (% dwb)	9.5

<sup>a</sup> As reported by the manufacturers.

TABLE II  
Properties of Polystyrene (PS) and Poly(methyl methacrylate) (PMA)<sup>a</sup>

Property	PS	PMA
Resin	Styron 695	04552
Specific gravity	1.04	1.19
Melt flow rate (200°C/5 kg)	1.5 g/10 min	NA <sup>b</sup>
Tensile modulus	397,000 MPa	NA
Molecular weight	NA	3,50,000
Glass transition temperature	NA	106°C

<sup>a</sup> As reported by the manufacturers.

<sup>b</sup> Not available.

## RESULTS AND DISCUSSION

### Radial Expansion Ratio

The effect of radiation on radial expansion ratio is shown in Figure 1. Radiation level had a significant ( $P > F = 0.001$ ) influence on radial expansion ratios. Maximum radial expansion ratio was obtained when samples were irradiated to 5 kGy. Further increases in radiation dosage resulted in decreased radial expansion ratios. Blocking over replicates ( $P > F = 0.5710$ ) and type of plastic used ( $P > F = 0.6488$ ) were effective. PS and PMS gave similar expansion ratios. Radial expansion ratios were significantly different at all levels of radiation except between 0 and 10 kGy. Sokhey and Chinnaswamy (1992), on the contrary, found increased expansion of 25% amylose starch extrudates with increasing radiation dosage but decreased expansion for 0% amylose starch. Higher expansion was attributed to degradation of starch chains and formation of cross links between chains which probably reduced the molecular size, resulting in increased expansion. However, Sokhey and Chinnaswamy (1992) used starches only and did not extrude plastics. Increased expansion in the present case also was probably due to increased degradation of starch and plastics. At higher dosages of irradiation, there was probably excessive alteration of molecular structure that increased cross-linking between starch chains or starch and plastics, thereby affecting the expansion.

### Bulk Density

Extrudate bulk density was influenced significantly ( $P > F = 0.001$ ) by level of radiation, but not by type of polymer. Figure 2 shows that the highest bulk densities were obtained at 30 kGy dosage. Lowest bulk density was obtained with 10 kGy which was not significantly different from the 5 kGy treatment. Bulk densities obtained with 0 and 20 kGy treatments were similar and significantly different from other radiation dosage levels. The bulk density results were consistent with expansion ratio trends.

### SME

Effect of radiation dosage on SME is shown in Figure 3. Maximum SME requirement was 146 kWh/kg at 0 kGy level, which was significantly higher than those for the 10, 20, and 30 kGy levels of radiation. The lowest SME requirement of 62 kWh/kg was required when the samples were subjected to 20 kGy radiation dosage before extrusion. The type of plastic did not significantly ( $P > F = 0.6488$ ) influence SME values, while level of radiation did have a significant ( $P > F = 0.001$ ) effect. At higher levels of radiation, there was probably too much cross-linking. This cross-linking possibly resulted in increased melt viscosity, which resulted in increased SME requirements.

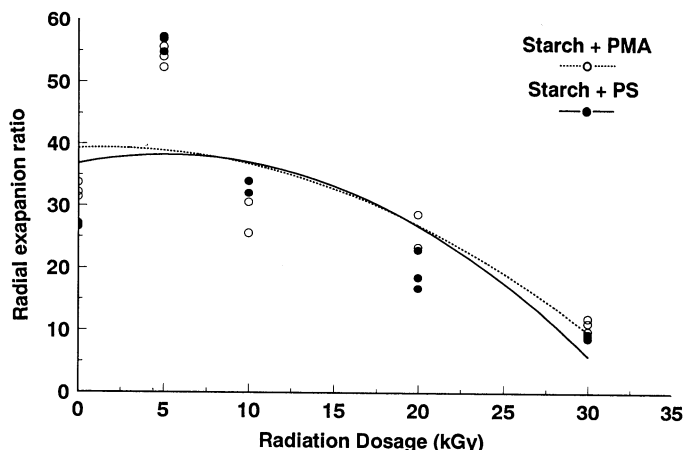


Fig. 1. Effect of radiation dosage on radial expansion ratio. PS = polystyrene. PMA = poly(methyl methacrylate).

## WSI

Native ungelatinized starches are normally insoluble in water, but extrusion increases the solubility of starches (Colonna et al 1989). Therefore, water solubility is a good indicator of the level of modifications or degradations of starch in extrudates. Figure 4 shows the effect of level of radiation on WSI. WSI was significantly influenced by the level of radiation. The lowest WSI of 10.64% was obtained with the 30 kGy dosage, while the 10 kGy exposure resulted in the maximum WSI of 27.7%. The type of polymer did not significantly affect the WSI. Sokhey and Chinnaswamy (1992) also reported increased solubility of extrudates with increasing radiation dosage and attributed it to increased degradation. In the present research, however, the water solubility decreased after 10 kGy, which we attribute to increased degree of cross-linking or grafting.

## Effect on Starch-Plastic Graft

From the results discussed here, it is clear that the various properties depended on the level of radiation dosage. At lower levels of radiation dosage, increased expansion ratio and solubility, and decreased bulk density and SME were observed. The trends reversed at higher levels of radiation. Whether these changes can be attributed to starch grafts or starch-plastic grafts needs to be determined. Starch plastic grafts are a combination of C<sup>12</sup>, mostly derived from synthetic polymers, and C<sup>13</sup>, mostly derived from corn starch. Mass spectral data were analyzed to determine the  $\delta^{13}\text{C}$  values in samples free from unreacted carbohydrates and unreacted plastics as outlined by Chinnaswamy and Hanna (1991) to ascertain the degree of graft qualitatively. Figure 5 shows the

effect of radiation dosage on  $\delta^{13}\text{C}$  value. Pure normal corn starch, PS, and PMA have a  $\delta^{13}\text{C}$  values of  $-10.5$ ,  $-28.4$ , and  $-31.27$ , respectively. When PS and PMA were mixed with starch, the  $\delta^{13}\text{C}\%$  value for starch decreased in proportion to the amount of plastic added. A physical mixture of starch and 10% PS gave a  $\delta^{13}\text{C}$  value of  $-12.5$ . When a physical mixture of starch and PS was extracted with chloroform, the  $\delta^{13}\text{C}$  value returned to  $-10.5$ . Thus, in this study, the  $\delta^{13}\text{C}$  value, after extraction of free polymer, was indicative of the degree of grafting.

Increasing the level of radiation resulted in significant ( $P > F = 0.001$ ) reductions in  $\delta^{13}\text{C}$  % values toward that of pure plastics, indicating better grafting. The lowest  $\delta^{13}\text{C}$  % value was obtained with 20 kGy, which was not significantly different from that obtained with 10 and 30 kGy, but significantly different from the 0 and 5 kGy irradiated samples, which had  $\delta^{13}\text{C}$  % values closer to that of pure starch. It was concluded that the number of grafted branches increased as the radiation was increased to 10 kGy. Beyond that, there was no significant increase in the number of grafted branches due to increased termination of the polymerization by the excess free radicals made available. Thus, the leveling off of the increase in starch-plastic grafts at higher dosage levels could be ascribed to depletion of both the free radicals and the availability of sites for free radicals to form starch-plastic grafts. But, it increased the cross-linking between the starch chains, which resulted in reduced expansion, increased bulk density, and reduced water solubility.

An important finding was that the functional properties were independent of the type of plastic polymer used so that PS can be substituted for by PMS, which is more environmentally friendly.

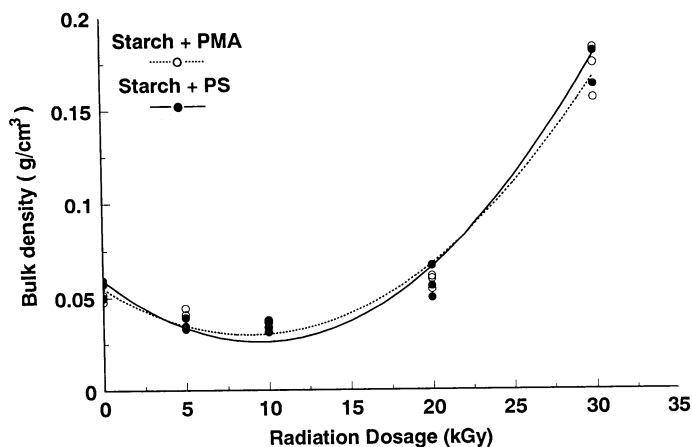


Fig. 2. Effect of radiation dosage on bulk density. PS = polystyrene. PMA = poly(methyl methacrylate).

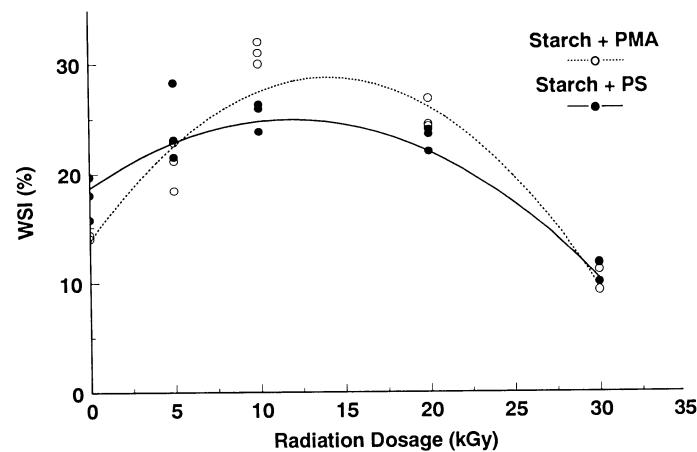


Fig. 4. Effect of radiation dosage on water solubility index (WSI). PS = polystyrene. PMA = poly(methyl methacrylate).

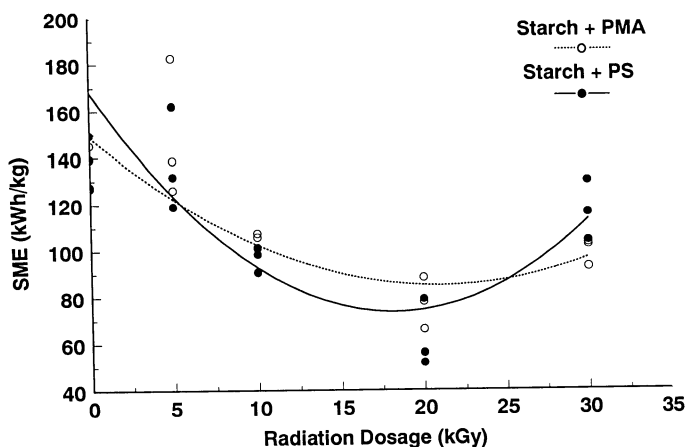


Fig. 3. Effect of radiation dosage on specific mechanical energy (SME). PS = polystyrene. PMA = poly(methyl methacrylate).

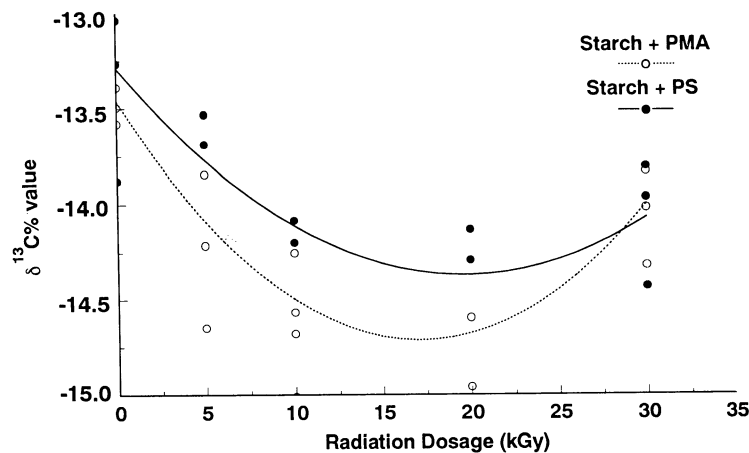


Fig. 5. Effect of radiation dosage on  $\delta^{13}\text{C}$  % value. PS = polystyrene. PMA = poly(methyl methacrylate).

## CONCLUSIONS

Irradiation of starch blended with 10% of either PS or PMA at different levels (0–30 kGy) and extrusion of the samples significantly influenced radial expansion ratio, bulk density, SME, WSI, and  $\delta^{13}\text{C}$  % values. Radiation at levels above 10 kGy resulted in leveling off of the starch-plastic graft formation. The properties studied were not influenced by the type of plastic used. Because PMA is more environmentally friendly it can be used in such grafts successfully without significantly affecting the physical attributes of the extrudates.

## ACKNOWLEDGMENTS

This research was funded by the United States Dept. of Agriculture.

## LITERATURE CITATIONS

- ADAMS, S. 1983. Recent advances in radiation chemistry of carbohydrates. Pages 149-170 in: *Recent Advances in Food Irradiation*. P. S. Elias and A. J. Cohen, eds. Elsevier Biomedical Press: Netherlands.
- BHATNAGAR, S., and HANNA, M. A. 1994. Amylose-lipid complex formation during single screw extrusion of various corn starches. *Cereal Chem.* 71:582-587.
- BHATNAGAR, S., and HANNA, M. A. 1995a. Physical, mechanical and thermal properties of starch based plastic foams. *ASAE Trans.* 38:567-571.
- BHATNAGAR, S., and HANNA, M. A. 1995b. Properties of extruded starch based plastic foams. *Ind. Crops Prod.* 4:71-77.
- CARR, M. E., KIM, S., YOON, K. J., and STANLEY, K. D. 1992. Graft polymerization of cationic methacrylate, acrylamide, and acrylonitrile monomers onto starch by reactive extrusion. *Cereal Chem.* 69:70-75.
- CHINNASWAMY, R., and HANNA, M. A. 1991. Extrusion-grafting of starch onto vinylic polymers. *Starch/Staerke* 43:396-401.
- COLONNA, P., TAYEB, J., and MERCIER, C. 1989. Extrusion cooking of starch and starchy products. Page 247 in: *Extrusion Cooking*. C. Mercier, P. Linko, and J. M. Harper, eds. Am. Assoc. Cereal Chem.: St. Paul, MN.
- FANTA, G. F. 1973. Block and Graft Copolymerization. R. J. Ceresa, ed. Wiley-Interscience: New York.
- FANTA, G. F., BURR, R. C., and DOANE, W. M. 1979. Graft polymerization of acrylamide and 2-acrylamido-2-methyl propane sulfonic acid onto starch. *J. Appl. Polym. Sci.* 24:2015-2023.
- FANTA, G. F., BURR, R. C., and DOANE, W. M. 1980. Polymerization of alkyl acrylates and alkyl methacrylates with starch. *J. Appl. Polym. Sci.* 25:2285-2294.
- GRANT, L. A., and D'APPLONIA, B. L. 1991. Effect of low level gamma radiation on water-soluble nonstarchy polysaccharides isolated from hard red spring wheat flour and bran. *Cereal Chem.* 68:651-652.
- HEBEISH, A., EL-ALFY, E., and KHALIL, M. I. 1988a. Synthesis of vinyl polymer-starch composites to serve as size base materials. *Starch/Staerke* 40:191-196.
- HEBEISH, A., EL-ALFY, E., and KHALIL, M. I. 1988b. Synthesis and properties of polyacrylamide starch graft copolymers. *Starch/Staerke* 40:223-229.
- MAHER, G. G. 1979. Grafting starch xanthate with vinyl monomers and hydrogen peroxide in foam rubber product. *J. Appl. Polym. Sci.* 24:9-17.
- PATIL, D. R., and FANTA, G. F. 1993. Graft copolymerization of starch with methyl acrylate: An examination of reaction variables. *J. Appl. Polym. Sci.* 47:1765-1772.
- RAYFORD, W. E., WING, R. E., and DOANE, W. M. 1979. Carboxyl containing starch graft polymer preparation and use in heavy metal removal. *J. Appl. Polym. Sci.* 24:105-113.
- ROPER, H., and KOCH, H. 1990. The role of starch in biodegradable thermoplastic materials. *Starch/Staerke* 42:123-130.
- SOKHEY, A., and CHINNASWAMY, R. 1992. Physicochemical properties of irradiation modified starch extrudates. *Food Structure* 11:361-371.
- SOKHEY, A. S., KOLLENGODE, A. N., and HANNA, M. A. 1994. Screw configuration effects on corn starch expansion during extrusion. *J. Food Sci.* 59:895-898,908.
- SWANSON, C. L., SHORGEN, R. L., FANTA, G. F., and IMAM, S. H. 1993. Starch-plastic materials—Preparation, physical properties, and biodegradability. *J. Environ. Polym. Degradation* 1:155-166.
- TRIMELL, D., and STOUT, E. I. 1980. Grafting acrylic acid onto starch and poly(vinyl alcohol) by photolysis. *J. Appl. Polym. Sci.* 25:2431-2434.
- YOON, K. J., CARR, M. E., and BAGLEY, E. B. 1993. Reactive extrusion vs. batch preparation of starch-g-polyacrylonitrile. *J. Applied Polym. Sci.* 45:1093-1100.

[Received January 18, 1996. Accepted May 14, 1996.]