

Irradiation-Modification of Starch-Containing Thermoplastic Blends. II. Rheological Studies

AMBUJ D. SAGAR,¹ MARCELO A. VILLAR,² EDWIN L. THOMAS,¹ ROBERT C. ARMSTRONG,³
and EDWARD W. MERRILL^{3,*}

¹Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, ²PLAPIQUI, Planta Piloto de Ingeniera Quimica, Bahia Blanca, Argentina, and ³Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts

SYNOPSIS

This study involves an examination of the changes in the rheological behavior (specifically the non-Newtonian viscosity) of blends of various starches with a synthetic polymer (polyethylene-co-vinyl alcohol) as a result of irradiation-modification. The results are generally consistent with fact that starch degrades substantially upon irradiation, while the synthetic polymer is relatively unaffected. However, the high-amylose starch-containing blends are less sensitive to irradiation than we would expect; this is attributed to possible interactions between the linear molecules from the high-amylose starch and the synthetic polymer.

© 1996 John Wiley & Sons, Inc.

INTRODUCTION

The use of starch in environmentally degradability thermoplastics for commercial applications has been the focus of some attention for many years. Although a number of different approaches have been attempted to utilize starch commercially for such applications, almost all have involved compounding starches in some form with synthetic thermoplastics. Generally, however, it is seen that the addition of starch to thermoplastics has adverse effects on the mechanical properties, as is evident from a lowering of the ultimate tensile strain and stress values for these blends as compared to the neat thermoplastics (e.g., Ramsay et al.¹). This should not be surprising, given the differences in the chemical nature and structure of starch in comparison to most thermoplastics (such as polyethylene) with which it is blended. Chemical modification of the starch previous to the blending,^{2,3} as well as the blending of starch with thermoplastics that can have improved chemical interactions with starch,^{4,5} have been explored in the past as possible routes to modify fa-

vorably the physical and mechanical properties of such blends. It has recently been shown that it is possible to modify the microstructure and mechanical properties of blends of starches with a synthetic polymer through physical and structural modification of the starch through irradiation.⁶ This study pertains to the changes in the rheological behavior, specifically the non-Newtonian viscosity of such irradiation-modified blends, since this property is of direct practical significance to the commercial processability of such blends. The experiments were carried out for a range of starch-synthetic polymer compositions and for different kinds of starches.

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 as follows: a waxy maize starch (Amioca), essentially 100% amylopectin, a native corn starch (Melojel), approximately 70% amylopectin and 30% amylose; and a physically modified high-amylose starch (EK Fl. Hylon VII), approximately 30% amylopectin and 70% amylose. These are subsequently referred to as WM, NC, and HY,

* To whom correspondence should be addressed.

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 paper. The details of the compounding and the electron-beam irradiation of these blends are presented elsewhere.⁶ Table I lists the glycerin and moisture contents as compounded, and also the moisture content after conditioning.⁷ The nomenclature of the blends is based on the starch type used in the blending, as well as its fraction in the dry feed. Therefore, the blend HY 70 contains 70% Hylon VII and 30% EVOH on a dry basis, with water and glycerin contents as indicated in Table I.

Rheological Measurements

The rheological measurements on the blends were obtained by using a capillary viscometer (Instron Model 3210 Rheometer coupled with a Model 4505 series Universal Testing Instrument), which consists basically of a barrel that can be heated and therefore can be used to melt the samples *in situ*, and a plunger. 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 was 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 min) to reach thermal equilibrium, conceivably due to better compaction and less loss of water. 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 applied to account for the non-Newtonian velocity profiles 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; $L/D = 66.7$) 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. Shear

Table I Water and Glycerin Contents of the Main Series of Starch/EVOH Blends as Compounded and As Conditioned (from Villar et al.⁷)

Blend	Glycerin Content (As Compounded)	Water Content (As Compounded)	Water Content (As Conditioned)
WM 100	16.1	7.8	9.5
WM 70	16.3	5.3	8.3
WM 50	14.8	9.0	7.1
WM 30	12.7	7.5	6.0
NC 100	12.2	15.8	9.8
NC 70	18.1	12.7	8.5
NC 50	16.1	9.9	6.9
NC 30	13.6	6.8	5.9
HY 100	15.1	8.7	8.1
HY 70	14.8	10.6	7.9
HY 50	15.6	12.1	7.5
HY 30	14.1	8.0	5.9
EVOH	14.1	0.3	6.9

rates of approximately $1\text{--}1000\text{ s}^{-1}$ were achievable in the experiments.

RESULTS AND DISCUSSION

Viscosity data for the pure components (with water and glycerin) after different irradiation dosages are shown in Figure 1. From our data on the 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) versus shear rate ($\dot{\gamma}$) curve stays almost unchanged [Fig. 1 (a)], except that at the higher shear rates where the viscosity seems to decrease 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),^a an increase in the viscosity in the low shear rate regime is 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. This is consistent with the limited literature on the effects of irradiation upon EVOH, which tend to indicate that although ionizing radiation does result in the formation of radicals in the solid polymer with subsequent coupling or decay reactions (with their con-

^a 200 kGys = 20 megarads.

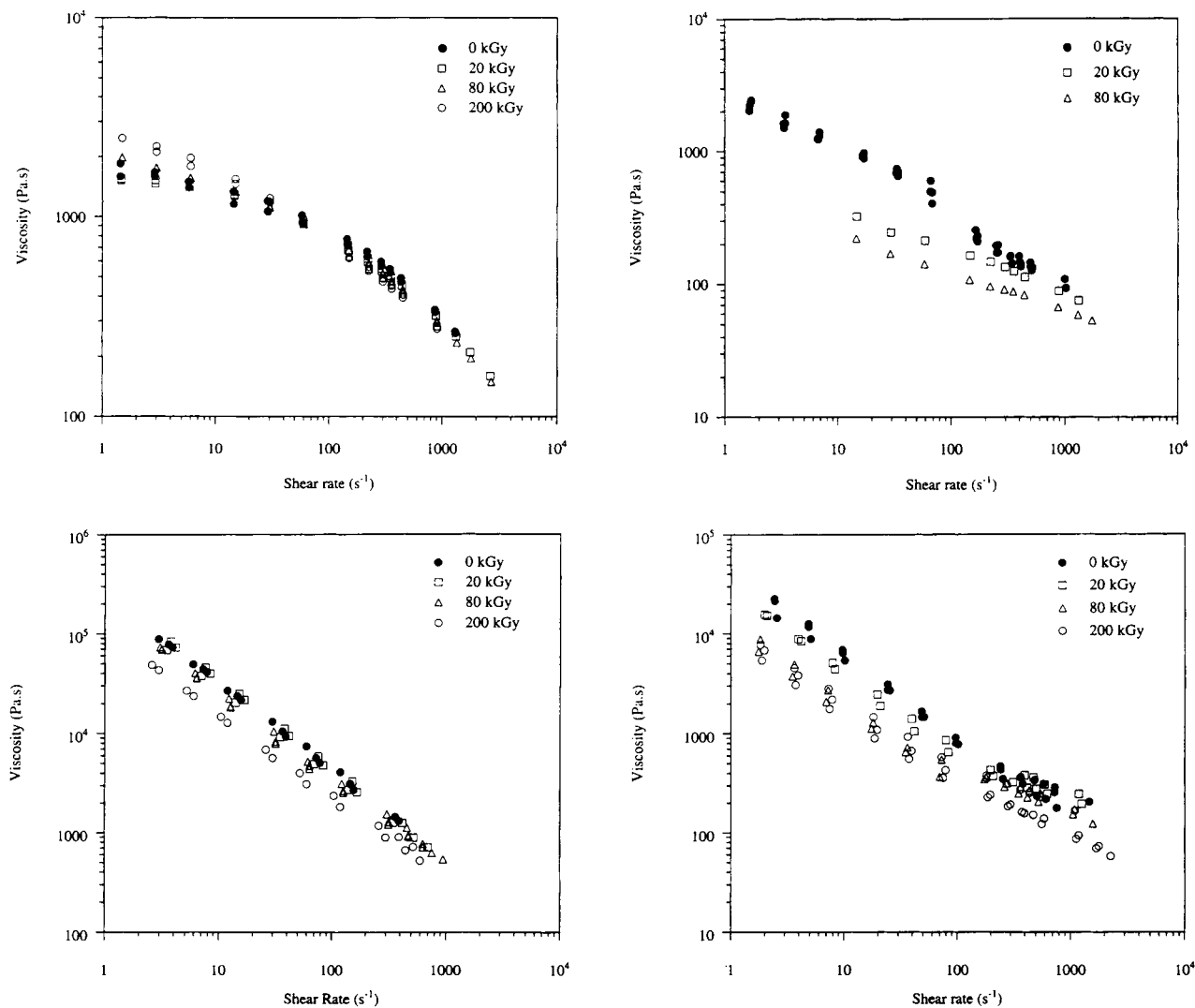


Figure 1 Influence of irradiation dosage on the viscosity of EVOH and neat starches (containing glycerin and water as noted in Table I): (a) EVOH, (b) WM 100, (c) HY 100, and (d) NC 100.

comitant cross-linking or degradative effects),^{8,9} overall EVOH tends to display only a limited sensitivity to irradiation, at least in the dose ranges relevant to our experiments.

The starches, on the other hand, show a notable decrease in the viscosity for all shear rates due to molecular scission [Fig. 1(b-d)], with the overall amount of the shift increasing monotonically with increased radiation doses. Again, this is consistent with the general observations in literature indicating the susceptibility of starch to ionizing radiation (e.g., Colonna et al.¹⁰) and with our own work on the chromatography of irradiated starches.⁶ There are, however, some difference among the rheological behavior of the various starch samples. For the waxy maize control sample [Fig. 1(b)], a discontinuity was observed in the η versus $\dot{\gamma}$ plot at a shear rate of about 60 s^{-1} that is presumably due to melt fracture. With a radiation dose of 20 kGys, this was eliminated, and a substantial reduction in the viscosity was seen at lower shear rates. At 80 kGys, 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 kGys 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. 1(c)], the viscosity was less affected by the irradiation treatment, with the 20 kGys 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. 1(d)], the behavior was 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 shear rate dependence of η showed power-law behavior that was very similar to that of the high-amylose starch and, at the higher 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; whereas 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. The 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, GPC

data indicate that the HY 100 samples suffer at least as much molecular scission as the WM 100 and the NC 100 samples.⁶ Such a difference between the melt viscosity and GPC results 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;¹¹ the HY 100 displays the formation of such complexes to a much greater extent than the NC 100.¹² 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 than the irradiated WM 100 or NC 100.

The viscosity of the control blends of starch with poly(ethylene-co-vinyl alcohol) has been shown to be vary with the relative fractions of the starch and the EVOH in the blend, as well as with the composition of the starch.⁷ For the irradiated materials, since the EVOH does not seem to be affected much by the radiation, changes in the viscosity of the irradiated blends generally follow the changes in the viscosity of the starch components. Accordingly, the waxy maize blends show the greatest overall reduction in viscosity [Fig. 2(a,b)], followed by the native corn [Fig. 3(a,b)]. The high-amylose blends showed the least reduction in viscosity [Fig. 4(a)]; 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 would not be easy to prove. In general, the magnitude of the changes increase with increasing amylopectin content for a given radiation dose.

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-rate viscosity of the blend should be a weighted log-addition of the zero-shear-rate viscosity of the individual fractions. Positive or negative deviation of the blend from this ideal behavior can give some insight into the interactions between the components. In the absence of zero-shear-rate data, it has been suggested that the assessment be carried out at constant shear rate or constant shear stress.^{13,14} The log-additivity rule at constant shear rates (Figs. 2-4) shows reasonable agree-

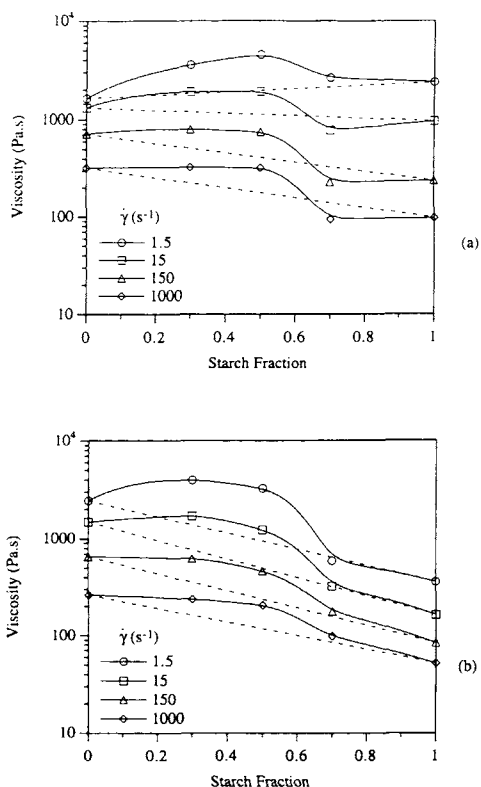


Figure 2 Viscosity of waxy maize/EVOH blends as a function of starch fraction (for fixed shear rate values): (a) control and (b) irradiated 200 kGys. Dashed line represents ideal mixing rule.

ment between measured and predicted η for all the samples.

CONCLUSIONS

The synthetic polymer used in these studies is not very radiation-sensitive (at least in the doses used in our experiments), and this is reflected in the relative insensitivity of the viscosity of this polymer to irradiation. Starch molecules, on the other hand, are significantly affected by ionizing radiation; this, in turn, has profound effects upon their rheological behavior. It is also seen that the high-amylose starch seems to be less sensitive to irradiation than the starches with high amylopectin content.

The effect of irradiation on the rheological behavior of the blends of the EVOH and the various starches is very much dependent upon the type of starch in ways not always expected. The blends containing waxy maize (and native corn to some extent) seem to behave rheologically like filled blends in which the EVOH acts as a matrix and

the fragmented starch granules (or starch-rich domains) as the filler within. Irradiation significantly disrupts the supramolecular as well as intramolecular structure of these starches and changes the rheological behavior of these blends, generally resulting in a lowering of the melt viscosity and the shear stresses at any given shear rate (consistent with the reduction of the size and intermolecular forces in the starch molecules due to irradiation).

The blends containing high-amylose starch display much higher viscosities than the high-amylopectin starch-containing blends, presumably due to the destructured nature of the precursor starch, as well as a predominance of linear amylose molecules. The change in the viscosity of the Hylon VII blends upon irradiation is counter-intuitive though. For some of the Hylon blends, the viscosity was sometimes higher than the control blends (even though, individually, the components displayed either almost no change or a reduction in viscosity upon irradiation). It is supposed that

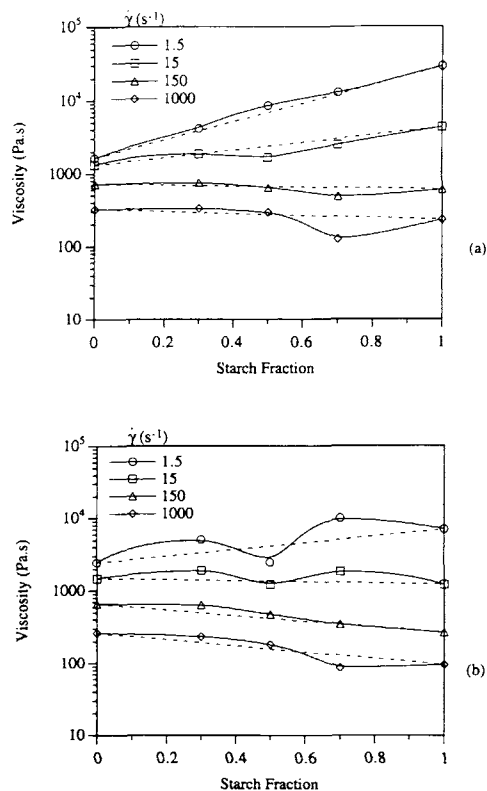


Figure 3 Viscosity of native corn/EVOH blends as a function of starch fraction (for fixed shear rate values): (a) control and (b) irradiated 200 kGys. Dashed line represents ideal mixing rule.

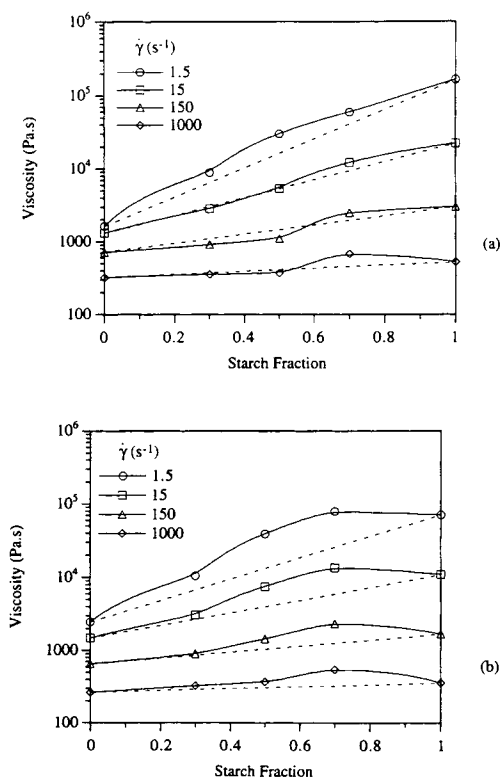


Figure 4 Viscosity of Hylon VII/EVOH blends as a function of starch fraction (for fixed shear stress values): (a) control and (b) irradiated 200 kGys. Dashed line represents ideal mixing rule.

this is due to some cross-linking between the amylose and the EVOH molecules (given their chemical structures and conformations, it is certainly possible that there could be some interaction between these molecules), though this hypothesis was not tested.

The processability of blends of synthetic polymer and starch is likely to improve if the starch is irradiated, primarily because of the macromolecular scission effected by the ionizing radiation which results in a lowering in the viscosity.

The financial support for this work was provided by the United States Department of Agriculture under Grant No. 91-COOP-2-6108.

REFERENCES

1. B. A. Ramsay, V. Langlade, P. J. Carreau, and J. A. Ramsay, *Appl. Environ. Microbiol.*, **59**, 1242 (1993).
2. R. L. Evangelista, Z. L. Nikolov, W. Sung, J.-L. Jane, and R. J. Gelina, *Ind. Eng. Chem. Res.*, **30**, 1841 (1991).
3. C. L. Swanson, R. P. Westhoff, and W. P. Doane, in *Proc. of the National Corn Utilization Conference II*, National Corn Growers Association, St. Louis, 1988.
4. B. T. Nwufu and G. J. L. Griffin, *J. Polym. Sci., Polym. Chem. Ed.*, **23**, 2023 (1985).
5. F. H. Otey, R. P. Westhoff, and W. M. Doane, *Ind. Eng. Chem. Res.*, **19**, 592 (1980).
6. A. D. Sagar, M. A. Villar, R. C. Armstrong, E. L. Thomas, and E. W. Merrill, *J. Appl. Polym. Sci.*, **61**, 139 (1996).
7. M. A. Villar, E. L. Thomas, and R. C. Armstrong, *Polymer*, to appear.
8. Y. Hama and T. Hirade, *Radiat. Phys. Chem.*, **37**, 59 (1991).
9. K. B. Ekman and J. H. Nasman, *J. Appl. Polym. Sci.*, **50**, 233 (1993).
10. P. Colonna, A. Buelon, and C. Mercier, in *Starch: Properties and Potential*, *Crit. Rep. Appl. Chem.*, **13**, T. Galliard, Ed., John Wiley, Chichester, 1987, pp. 79-114.
11. T. Galliard and P. Bowler, in *Starch: Properties and Potential*, *Crit. Rep. Appl. Chem.*, **13**, T. Galliard, Ed., John Wiley, Chichester, 1987, pp. 55-78.
12. S. Simmons, pers. commun., June 2, 1994.
13. L. A. Utracki, *Polymer Alloys and Blends: Thermodynamics and Rheology*, Hanser, Munich, 1990.
14. L. A. Utracki, *Polym. Eng. Sci.*, **23**, 602 (1983).

Received April 4, 1995

Accepted for publication January 5, 1996