

γ -Radiation-Treated Starch/Poly(vinyl alcohol) Composites for Cotton Fabric Sizing

Abdel-Wahab M. El-Naggar, Magdy M. Senna, Salwa A. Khalil

Radiation Chemistry Department, National Center For Radiation Research and Technology, P.O. Box 29, Nasr City, Cairo, Egypt

Received 19 May 2003; accepted 3 August 2003

ABSTRACT: Films of different composites based essentially on maize starch (MS)/poly(vinyl alcohol) (PVA) blends were prepared by the solution-casting technique and subjected to various doses (20–100 kGy) of γ -radiation. The MS/PVA blends were modified by the addition of glycerol (GY) and a graft copolymer (GP) of MS with acrylamide separately or together with the polymer blend solutions before casting. The γ -treated composites were evaluated in terms of the apparent viscosity and their suitability as sizing materials for cotton fabrics. The sizeability of these composites for cotton fabrics was assessed in terms of the size removal percentage at different temperatures and the effect on the tensile properties and water absorption. The change

in the apparent viscosity with the shear rate showed that γ -irradiation improved the behavior of MS/PVA blends and their composites with GY or GP as a sizing material for cotton fabrics. Moreover, the improvement in the tensile mechanical properties of the sized cotton fabrics with these composites gave further support to this finding. The results for the size removal percentage and water adsorption indicated that these composites could be removed by washing at 70°C for 10 min. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 3818–3826, 2004

Key words: blends; composites; radiation

INTRODUCTION

Sizing is a process in which specific materials in aqueous solutions are applied to warp yarns as a protective coating to withstand the movement of yarns and abrasive mechanical stresses during weaving. Many materials are used as sizing materials, such as starches, poly(vinyl alcohol) (PVA), gums, carboxymethylcellulose, gelatins, and synthetic polymers and copolymers.¹ Of these materials, starch and PVA are the most important polymers often used in the sizing process. Synthetic polymers work best on filament yarns. Meanwhile, starches are important base materials used for cotton sizing because of their cheap price, abundance, and ease of application. However, natural starches are not soluble in cold water, and so cooking is necessary to get the granules to form a homogeneous solution. Another problem with starch sizing materials is the retrogradation process, in which, if the concentration of the starch solution becomes concentrated by the evaporization of water and/or cooling, an irreversible gel is formed that will not redisperse.² The problem encountered in the desizing of natural starches is that once a cooked starch solution dries, the resulting film will not easily redissolve in water. Thus, for the complete removal of starch from a fabric, te-

dious and expensive chemical methods are being used, such as enzymes, acid hydrolysis, and oxidation.³ However, one of the advantages of PVA is that the dried films will redissolve in water without degradation. However, the problem with PVA is the effect of heat setting, which occurs when the desizing process is carried out at a high temperature.⁴

As noted, both starches and PVA cause problems in the sizing and desizing processes. Hebeish and co-workers carried out extensive work on modifying the physicochemical properties of starches: starches were acid-treated,⁵ oxidized,^{6–8} etherified,⁹ and grafted by chemical methods.¹⁰ The blending of starch with PVA¹¹ or poly(methacrylic acid)¹² has been also investigated for the property modification of natural starches. However, most research work on polymer blends based on starch and PVA has been directed to the preparation of biodegradable plastics for environmental reasons.^{13–15}

It is interesting to investigate the effect of high-energy radiation on the chemical and physical properties of synthetic polymers and starches.^{16–19} An earlier report studied the effect of γ -irradiation on the digestibility of raw starch for radio sterilization for uncooked starch fermentation.²⁰ The importance of these effects arises from the fact that high-energy radiation can induce chain scission and crosslinking.

This work was undertaken to investigate the sizeability of different composites based on maize starch (MS)/PVA blends before and after γ -irradiation. The suitability of these composites as sizing materials was

Correspondence to: A.-W. M. El-Naggar (ab_nagga@yahoo.com).

investigated in terms of the viscosity changing with the shear rate, whereas the efficiency of these materials as sizing materials for cotton fabrics was studied in terms of the size removal efficiency, mechanical properties, and water absorption.

EXPERIMENTAL

Materials

MS was supplied by the Egyptian Company for Starch and Glucose (Cairo, Egypt). The partially hydrolyzed PVA (laboratory-grade) was in the form of a powder, had a weight-average molecular weight of 125,000, and was obtained from Laboratory Rasayan (India). Acrylamide monomer (AM) with a purity of more than 99% (gas chromatography) was obtained from Merck (Germany). All other chemicals were pure and were used as received.

Preparation of starch/PVA composites

Basically, four MS/PVA composites were prepared as films by the solution-casting technique. The first composite was based on MS/PVA blends at different ratios. It was prepared by the dissolution of MS powder in water with continuous stirring and heating at 80°C for an hour until complete gelatinization. The required amount of PVA dissolved in hot water was added with continuous stirring. The films obtained by casting were allowed to dry in air and then were placed in a vacuum oven at 80°C for the removal of residual water. For the second and third composites, glycerol (GY) and a graft copolymer (GP) were added to the first blend solutions at constant concentrations of 10 and 5%, respectively. The GP was prepared by the direct radiation grafting method, in which both MS and AM were simultaneously exposed to γ -radiation in sealed tubes with water as a solvent. The MS GP was removed, filtered, washed with water, and extracted with water for the removal of the homopolymer and was dried in a vacuum oven at 80°C. The grafting yield was determined by elemental analysis for nitrogen content. The fourth composite was prepared by the addition of a mixture of GY and GP to MS/PVA blend solutions at 10 and 5%, respectively.

γ -Irradiation

Irradiation in the required doses was performed in a Co 60 γ cell (Issle Bovatel, Russia) at a dose rate of 7.64 kGy h⁻¹ in air.

Rheological measurements

The rheological properties of MS/PVA composites before and after γ -irradiation were measured with a

Brookfield (England) DV-III-Rv with an SC4-21 spindle. The measurements were performed at a shear rate between 177 and 233 s⁻¹ and at 90°C. The apparent viscosity [η (cP)] was calculated as follows:

$$\eta = (t/D) \times 1000$$

where t is the shear stress (dyn/mm) and D is the rate of shear (S⁻¹).

Sizing and desizing procedures

Aqueous slurries (10%) of the different MS/PVA composites films before and after γ -irradiation were cooked at 90°C for 20 min. Unprocessed cotton fabric samples were impregnated in the cooked composites; this was followed by squeezing to a content of approximately 100% and drying at 100°C for 5 min. The sized cotton samples were then evaluated in terms of the tensile strength and elongation at break. The desizing process was carried out by the washing of the sized cotton samples in water at different temperatures in the presence of a wetting agent for 10 min. The loss in the fabric weight after washing is called *size removal*, and it is determined as follows:

$$\text{Size removal (\%)} = [(W_0 - W_1)/W_0] \times 100$$

where W_0 and W_1 are the sized cotton sample weights before and after washing, respectively.

Mechanical measurements

Mechanical tests, including the tensile strength, elongation at yield, and break points, were performed at room temperature with an Instron model 1195 machine, which applied a crosshead speed of 10 mm/min. For this test, the fabrics were cut into rectangular stripes 20 cm long and 5 cm wide. The recorded value for each mechanical parameter was the average of five measurements taken according to ASTM standards.

Water absorption properties

The efficiency of size removal (desizing) was evaluated in terms of the static water absorption test according to AATCC Test Method 21-1972. Static absorption involves the immersion of conditioned desized cotton samples of weight W_0 , fastened on one side to a sinker, in a vessel full of distilled water for 20 min, removal, and reweighing (W_2); the percentage of absorbed water is determined as follows:

$$\text{Water absorption (\%)} = [(W_2 - W_0)/W_0] \times 100$$

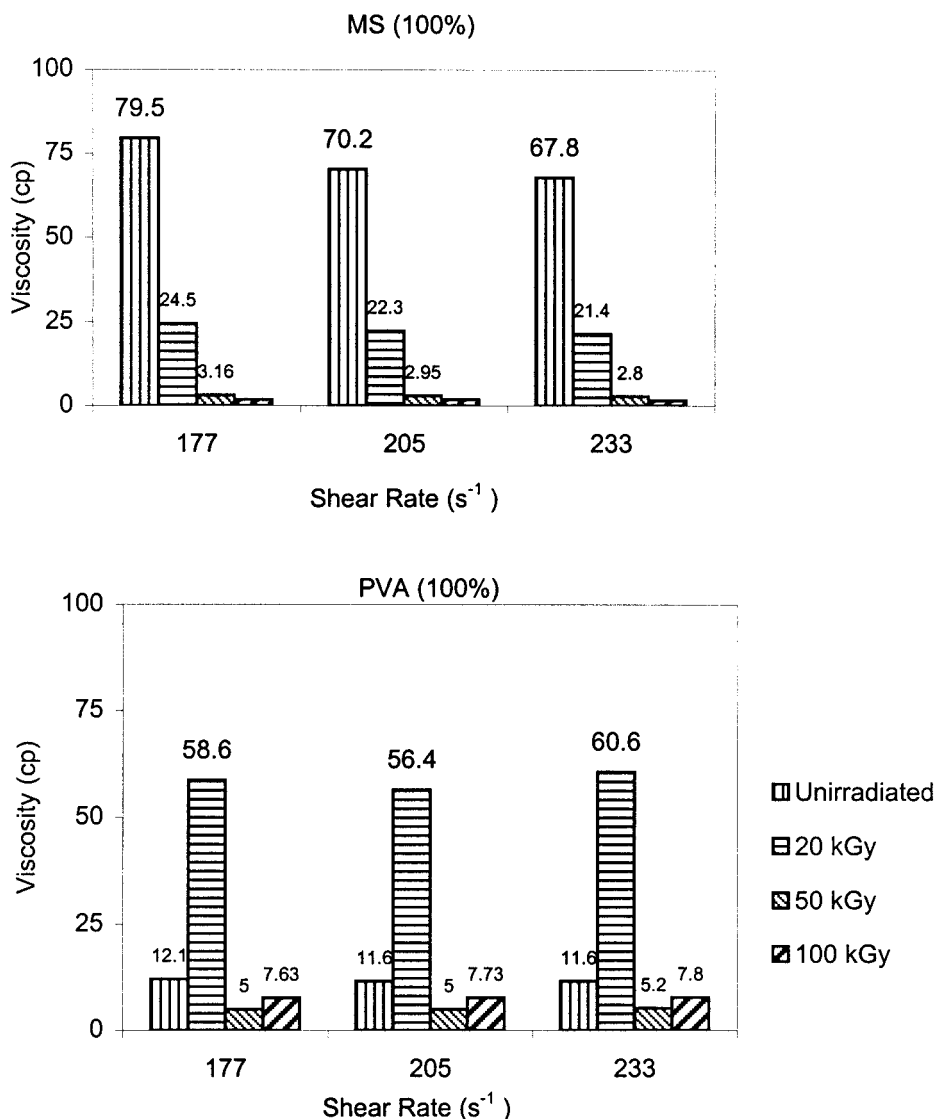


Figure 1 Apparent viscosity at different shear rates for pure MS and PVA homopolymers before and after various doses of γ -irradiation.

RESULTS AND DISCUSSION

For a practical and good sizing material, the solution viscosity during preparation should remain constant or increase as the shear rate increases. Moreover, general requirements include flexibility, abrasion resistance, and good adhesion. Most importantly, the material should be easily removed from the fabrics during the desizing process.

Viscosity of γ -irradiated MS/PVA composites

Pure MS and PVA homopolymers

Figure 1 shows the apparent viscosity at different shear rates of pure MS and PVA homopolymers before and after various doses of γ -irradiation. The unirradiated MS possessed a higher viscosity than PVA at any

shear rate. The apparent viscosity of unirradiated MS decreased as the shear rate increased, whereas that of PVA seemed to remain unchanged with the shear rate. The apparent viscosity of MS was greatly reduced as the irradiation dose increased because of oxidative degradation. The apparent viscosity of PVA suddenly increased at a dose of 20 kGy and then decreased at higher doses. However, γ -irradiated PVA seemed to behave as a Newtonian fluid; that is, the viscosity remained unchanged as the rate of shear increased. A similar behavior was observed for γ -irradiated MS in agreement with previous work.¹⁹

MS/PVA blends (composite I)

The change in the apparent viscosity as a function of the shear rate for different MS/PVA blends, before and after

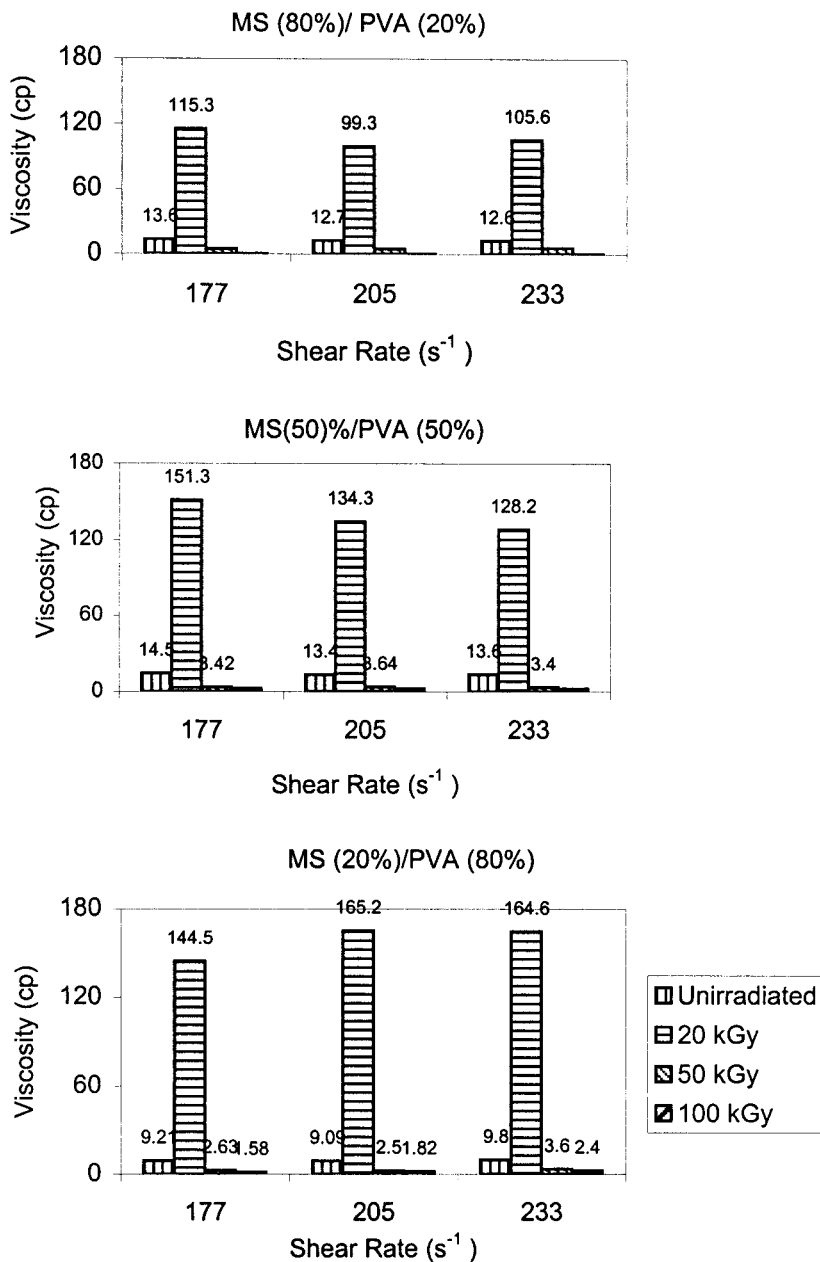


Figure 2 Apparent viscosity at different shear rates for MS/PVA blends of different compositions before and after various doses of γ -irradiation.

γ -irradiation, is shown in Figure 2. The blending of PVA, with an initially low apparent viscosity, clearly resulted in blends with a very low apparent viscosity. Similarly to pure PVA, a sudden increase in the apparent viscosity of the MS/PVA blends was observed at a dose of 20 kGy and then greatly decreased at 100 kGy. At any irradiation dose, the apparent viscosity of the MS/PVA blends increased or almost remained constant with an increasing rate of shear. These findings were clear for the MS/PVA blends rich in MS or PVA, in which the apparent viscosity increased with an increasing rate of shear. This behavior indicated the presence of mechanical hindrance of the particles in the concentrated suspensions, by

which the particles were packed together with a large deforming force into a solid complex in agreement with previous work.¹⁹ Thus, the blending of MS and PVA, followed by γ -irradiation, changed the behavior of the blends from a pseudoplastic fluid to a dilatant. The sudden increase in the apparent viscosity of pure PVA or its blends with MS at 20 kGy was probably due to crosslinking.

MS/PVA/GY (composite II)

GY is usually added as a plasticizer to starch polymer in many formulations to modify its properties.^{21,22}

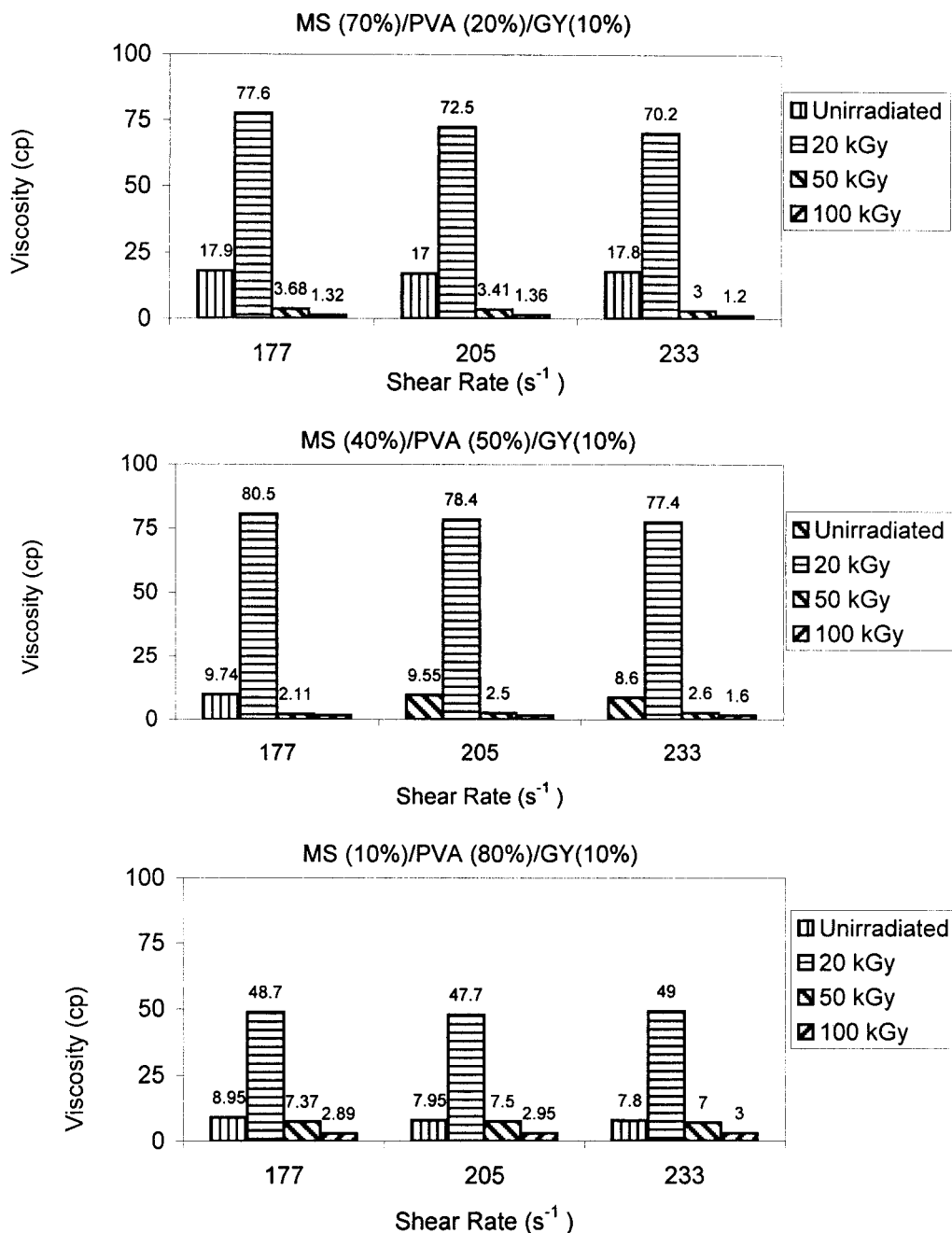


Figure 3 Apparent viscosity at different shear rates for different MS/PVA/GY composites before and after various doses of γ -irradiation.

This modification is due to the interaction of starch with GY and, therefore, prevents the retrogradation process that occurs in starch with aging. The effect of GY on the apparent viscosity of MS/PVA blends is shown in Figure 3. The addition of GY increased the apparent viscosity of the unirradiated MS/PVA polymer blends, regardless of the change in the rate of shear (Fig. 2). When the rate of shear increased from 177 to 233 s⁻¹, the apparent viscosity of the unirradiated MS/PVA/GY composites seemed to remain constant, regardless of the irradiation dose; this indicated

stability in the rheology of such composites. In comparison, the MS/PVA/GY composites were better than MS/PVA blends without GY from the point of view of sizing materials.

MS/PVA/GP and MS/PVA/GP/GY (composites III and IV)

The effect of GP of MS with acrylamide alone or with GY as an additive on the apparent viscosity of an MS (20%)/PVA (80%) blend at different shear rates before

TABLE I
Effect of GY and MS GP (with acrylamide) Additives on the Apparent Viscosity at Different Shear Rates of an MS (20%)/PVA (80%) blend

Composite	Shear rate (s ⁻¹)	Viscosity (cP)			
		Not irradiated	20 kGy	50 kGy	100 kGy
MS/PVA/GP	177	8.95	188.90	7.37	2.89
	205	7.95	194.80	7.50	2.95
	233	7.80	201.30	7.00	3.00
MS/PVA/GP/GY	177	36.70	56.10	28.20	11.60
	205	35.00	60.00	28.90	11.10
	233	34.30	65.20	32.70	11.80

Concentration of GY-10%; concentration of GP-5%, based on the polymer blend weight.

and after various doses of γ -irradiation is shown in Table I. GY was added at a constant concentration of 10%, whereas GP was added at a concentration of 5%; both concentrations were based on the weight of the blend. Also, the graft yield of acrylamide onto MS, as determined by elemental analysis for nitrogen content, was found to be 15%. The addition of GP had nearly no effect on the apparent viscosity of the unirradiated MS/PVA blend. However, when GY and GP were added to the MS/PVA blend, the apparent viscosity was greatly increased. A sudden increase in the apparent viscosity at 20 kGy was also found for the two composites containing GP alone or a mixture of GP and GY. When the irradiation dose increased from 20 to 100 kGy, a sudden drop to very low values was observed, particularly for the blend containing only GP.

The behavior of composites III and IV as Newtonian fluids [i.e., the stability of the apparent viscosity or an increase with an increasing rate of shear (dilatant)] largely depended on the irradiation dose. In this respect, composites III and IV behaved as Newtonian fluids over the studied range of irradiation doses, whereas the unirradiated composites were not suitable as sizing materials. This was because the apparent viscosity of the unirradiated composites tended to decrease as the rate of shear increased.

On the basis of the results for the viscosity of the four MS/PVA composites, a few points may be made:

1. When the shear rate increased from 177 to 205 S⁻¹ or from 205 to 233 S⁻¹, the apparent viscosity of unirradiated pure PVA, MS/PVA blends, MS/PVA/GY, and MS/PVA/GP remained unchanged or increased with increasing shear rates; this indicated their suitability as sizing agents. However, unirradiated MS and MS/PVA/GP/GY materials were not suitable as sizing agents.
2. γ -Radiation seemed to alter the nature of the unsuitable composites as sizing agents to a practical nature in which the apparent viscosity increased with the shear rate.
3. According to the previous results, it may be concluded that the best composites as sizing agents were MS/PVA/GY and MS/PVA/GP/GY irradiated to 50 and 20 kGy, respectively.

Sizeability of γ -irradiated MS/PVA composites

The efficiency of the sizing process mainly depends on the type of yarn to be sized, the sizing base material, and the compatibility between them. The sizeability of the different MS/PVA composites was evaluated in terms of the mechanical properties of sized fabrics, the size removal percentage (desizing), and the water absorption of the desized fabrics.

Tensile mechanical properties

The tensile mechanical properties of cotton fabrics sized with the different γ -irradiated MS/PVA composites are shown in Table II. On the basis of the results, a few points may be made:

1. The untreated cotton fabrics and cotton fabrics treated with unirradiated composites III and IV showed the stress-strain behavior of brittle polymers, in which no yielding was observed. However, cotton fabrics treated with unirradiated composites I and II displayed the stress-strain behavior of tough polymers with yielding properties. These trends can be explained by the viscosities of the different composites. In this respect, low-viscosity solutions eventually penetrated the yarns more easily than high-viscosity solutions. As a result, sizing with high-viscosity solutions increased the breaking stress and strain, whereas the penetration of low-viscosity solutions changed the nature of the yarns and increased the elasticity of the fabrics.
2. Cotton fabrics treated with γ -irradiated composites showed yielding properties, regardless of the MS/PVA composite. The oxidative degradation of MS caused by irradiation eventually reduced

TABLE II
Tensile Mechanical Properties of Cotton Fabric Sized with Different γ -Irradiated MS/PVA Composites as Sizing Materials

Sizing composite	Irradiation dose (kGy)	Yield stress (MPa)	Yield strain (%)	Breaking stress (MPa)	Breaking strain (%)
Untreated MS/PVA (I)	Unirradiated	None	None	4.3 ± 0.20	9.4 ± 0.20
	Unirradiated	3.4 ± 0.5	2.8 ± 0.30	6.9 ± 0.6	16.3 ± 1.1
	20	6.4 ± 0.8	2.0 ± 0.10	6.2 ± 0.4	11.8 ± 0.9
	50	None	None	6.1 ± 0.31	10.9 ± 0.7
MS/PVA/GY (II)	100	None	None	6.0 ± 0.38	10.0 ± 2.0
	Unirradiated	33.4 ± 1.9	13.9 ± 1.3	35.6 ± 6.5	16.7 ± 0.4
	20	29.5 ± 2.1	11.2 ± 0.7	30.7 ± 4.5	13.6 ± 0.7
	50	24.5 ± 2.2	2.2	30.4 ± 6.2	11.3 ± 0.7
MS/PVA/GP (III)	100	15.5 ± 3	2.1 ± 0.10	28.5 ± 3.2	9.9 ± 0.5
	Unirradiated	None	None	5.2 ± 0.10	12.1 ± 1.4
	20	6.5 ± 0.3	2.8 ± 0.4	6.3 ± 0.2	12.1 ± 1.2
	50	6.0 ± 0.70	6.3 ± 0.3	6.5 ± 0.6	12 ± 1.3
MS/PVA/GP/GY (IV)	100	None	None	7.4 ± 0.3	9.8 ± 0.4
	Unirradiated	None	None	33.1 ± 5.4	11.8 ± 0.3
	20	15.5 ± 0.2	3.3	29.1 ± 3.2	9.3 ± 0.7
	50	14.3 ± 0.50	4.5 ± 0.20	27.9 ± 2.5	8.6 ± 0.4
	100	6.4 ± 0.30	2.0	22.8 ± 1.1	8.0 ± 0.2

The blend used in all composites was MS (80%)/PVA (20%).

the viscosity and, therefore, increased the penetration of the yarns.

- Sizing with unirradiated MS/PVA(I) caused an increase in the breaking stress of cotton fabric by approximately 60%, whereas the increase was approximately 21% with the unirradiated MS/PVA/GP composite. However, the treatment with unirradiated MS/PVA/GY and MS/PVA/GY/GP composites increased the breaking stress of cotton fabric by approximately 730 and 670%, respectively, based on the untreated fabric (control).
- The application of γ -irradiated composites increased the break strain of cotton fabrics.
- In summary, the tensile mechanical properties of cotton fabrics treated with unirradiated or γ -irradiated composites were much higher than those of untreated cotton.

The improvement in the tensile mechanical properties could be attributed to the formation of thin films of polymer blend composites surrounding the yarns and hence an increased ability to withstand load under tension. Moreover, all the composites were hydrophilic in nature, and so the adhesion to cotton fabric was strong enough to resist breaking or cracking under tension.

Size removal percentage

After a sizing solution is applied to fabrics and dried, the resulting coatings have to be removed to meet the requirements of aftertreatment processes such as bleaching and dyeing. Thus, the efficiency of the de-

sizing process was evaluated to determine the size removal percentage at different temperatures for 10 min for the different γ -irradiated MS/PVA composites, as shown in Table III. In the textile industry, the desizing process of starches is often carried out under the effect of enzymes for at least 6 h to ensure that all starches are converted into low-molecular-weight polysaccharides, which are soluble in water. However, boiling water is still needed to remove the residual

TABLE III
Size Removal Percentage at Different Temperatures of Unirradiated and Irradiated MS/PVA Composites After They Had Been Applied to Cotton Fabrics

Sizing composite	Irradiation dose (kGy)	Size removal (%)		
		50°C	70°C	80°C
MS/PVA (I)	Unirradiated	53.22	72.7	83.91
	20	70.13	94.16	85.04
	50	76.24	95.91	97.15
	100	99.13	100	100
MS/PVA/GY (II)	Unirradiated	81.14	83.30	79.51
	20	93.08	96.85	80.98
	50	98.13	100	95.26
	100	98.65	100	94.02
MS/PVA/GP (III)	Unirradiated	85.6	92.46	51.56
	20	86.63	92.49	87.09
	50	91.74	95.07	88.11
	100	95.29	94.10	96.43
MS/PVA/GP/GY (IV)	Unirradiated	91.95	87.83	85.31
	20	94.03	98.89	92.02
	50	95.64	98.19	93.86
	100	92.78	97.21	94.32

The concentrations of GY and GP are the same as in Table I. The blend used in all of the composites was MS (80%)/PVA (20%).

TABLE IV
Water Absorption at Different Periods of Cotton Fabrics After the Desizing Process of Different MS (20%)/PVA (80%) Composites Subjected to a Dose of 50 kGy of γ Irradiation

Sizing composite	Water absorption (%)				
	1/2 h	1 h	2 h	3 h	24 h
Untreated	30.33	54.93	55.32	56.72	57.00
MS/PVA (I)	70.82	87.16	88.05	94.57	105.52
MS/PVA/GY (II)	75.14	91.52	95.65	100	115.23
MS/PVA/GP (III)	70.50	81.75	87.79	100	108.46
MS/PVA/GP/GY (IV)	82.63	89.26	94.24	100	100

The concentrations of GY and GP are the same as in Table I.

starches. In general, the size removal percentage increased as the temperature of the desizing process increased from 50 to 70°C, regardless of the kind of composite. When the temperature of the desizing process was increased to 80°C, the size removal percentage of most composites decreased, and this indicated the effect of heat setting.⁴ The desizing of γ -irradiated composites was clearly easier than that of unirradiated composites. In this respect, a nearly complete removal of all the γ -irradiated composites (50–100 kGy) was observed at 70°C.

Water absorption of desized fabrics

The water absorption of fabrics may be considered to be one of the most important properties in textile processing because all the aftertreatment processes have to be carried out in aqueous solutions. Therefore, as much as the sizing process is necessary in the weaving step, the removal of these materials is more important; otherwise, deposition inside the voids of the fibers would cause many problems.

Table IV presents the results of water absorption at different times for cotton fabrics after the desizing of different MS/PVA composites initially subjected to a dose of 50 kGy of γ -irradiation. The desizing process was carried out at 70°C for 10 min with solutions containing the MS/PVA composites and a 1% wetting agent, similarly to the industry. Also, the untreated fabric was treated with the same solution under identical conditions, except for the sizing composites. The results clearly indicated that the different MS/PVA composites were soluble in hot water and were completely removed. Moreover, the cotton fabrics absorbed approximately 100% water after a period of 3 h. Therefore, the desized fabric was amenable to aftertreatment processes such as dyeing and finishing. Composites with GY apparently improved the wettability of cotton fabric, in addition to their function as sizing materials, more than the pure MS/PVA blends and the composites containing GP. The relatively improved water absorption of untreated cotton fabric

was due to the action of the wetting agent at the relatively high temperature of the desizing process.

CONCLUSIONS

An efficient sizing agent is one whose viscosity behaves as a Newtonian fluid; that is, it is independent of the shear rate or increases as the shear rate increases (dilatant) during the preparation of the sizing solution. In this work, the viscosity/shear-rate relationship and the sizeability of different composites based on polymer blends composed of MS and PVA, before and after γ -irradiation, were studied. In this respect, GY as a plasticizer and GP as a compatibilizing agent were added to the polymer blend solutions to obtain different composites. In general, γ -radiation was demonstrated to be an effective tool for changing the different composites into efficient sizing materials. γ -Irradiation changed the behavior of pure MS/PVA blends from a pseudoplastic fluid to a dilatant fluid. MS/PVA/GY composites, before and after γ -irradiation, showed the behavior of Newtonian fluids, being independent of the shear rate and irradiation dose. However, blends with GY were better than pure MS/PVA blends. According to the obtained results, the best composites as sizing agent were MS/PVA/GP and MS/PVA/GY/GP composites irradiated to 50 and 20 kGy, respectively. The sizeability studies, in terms of the tensile properties, size removal, and water absorption of cotton fabrics sized with the different composites, indicated the following points: (1) the tensile mechanical properties of treated fabrics with unirradiated or irradiated composites were much higher than those of untreated fabrics, (2) the size removal of irradiated composites was easier than that of unirradiated ones, and (3) the desized cotton fabrics were amenable to aftertreatment processes such as dyeing and finishing.

References

- Davidson, R. L. In *Handbook of Water-Soluble Gums and Resins*; Crawford, H. B.; Kowalczyk, T. G., Eds.; McGraw-Hill: New York, 1980.

2. Takaya, T.; Sano, C.; Nishinari, K. *Carbohydr Polym* 2000, 4, 197.
3. Trotman, E. R. *Dyeing and Chemical Technology of Textile Fibers*; Carless Griffin: London, 1975.
4. Charles, T. *Chemistry & Technology of Fabric Preparation & Finishing*; NC, 1992.
5. Hebeish, A.; Abdel-Thalouth, I.; Ibrahim, M. A.; El-Zairy, M. R. *Starch* 1985, 37, 273.
6. Hebeish, A.; El-Sisi, F.; Abdel-Hafize, S. A.; Abdel-Rahman, A. A.; El-Rafie, M. H. *Starch* 1992, 44, 388.
7. Hebeish, A.; El-Rafie, M. H.; El-Sisi, F.; Abdel-Hafize, S. A.; Abdel-Rahman, A. A. *Polym Degrad Stab* 1994, 43, 363.
8. Abdel-Hafize, S. A. *Polym Degrad Stab* 1995, 47, 275.
9. Hebeish, A.; Bayazeed, A.; El-Alfy, E.; Khalil, M. I. *Starch* 1988, 40, 223.
10. Hebeish, A.; Ragheb, A. A.; El-Rafai, R.; Saad, M. A.; Abdel-Thalouth, I. *Starch* 1992, 46, 109.
11. Hebeish, A.; El-Rafie, M. H.; Higazy, A.; Ramadan, M. A. *Starch* 1992, 44, 101.
12. Hafiz, A. *Polym Degrad Stab* 1997, 55, 9.
13. Peter, J. S.; Jean, M. M.; Mark, J. H.; Elizabeth, A. C.; David, L. K. *Polym Prepr (Am Chem Soc Div Polym Chem)* 1992, 33, 139.
14. Ambuj, D. S.; Marcelo, A. V.; Edwin, L. T.; Robert, C. A.; Edward, W. M. *J Appl Polym Sci* 1996, 61, 139.
15. Lrcks, J. *Polym Degrad Stab* 1998, 59, 245.
16. Senna, M. M.; Aly, H. A.; Ali, Z. I.; El-Naggar, A. M. *Polym Degrad Stab* 2001, 71, 53.
17. El-Naggar, A. M.; Lopez, L. C.; Wilkes, G. L. *J Appl Polym Sci* 1990, 39, 427.
18. El-Naggar, A. M.; Kim, H. C.; Lopez, L. C.; Wilkes, G. L. *J Appl Polym Sci* 1989, 37, 1635.
19. Hebeish, A.; El-Naggar, A. M.; El-Sisi, F.; Abdel-Hafize, S. A.; El-Salmwi, K. *Polym Degrad Stab* 1992, 36, 249.
20. Tume, T.; Tamura, N. *Starch* 1992, 44, 101.
21. Carr, M. E. *J Appl Polym Sci* 1991, 42, 45.
22. Jeroen, J. G.; Remko, C. B.; Dick, D. W.; Johannes, F. G. *Ind Crops Prod* 1996, 5, 1.