ELSEVIER

PII: S0144-8617(96)00019-7

Carbohydrate Polymers 31 (1996) 157–160

0144-8617/96/$15.00 + .00

Studies on *Chenopodium quinoa* and *Amaranthus paniculatas* starch as biodegradable fillers in LDPE films

N. Thoufeek Ahamed,[a] R.S. Singhal,[a] P.R. Kulkarni,[a] D. D. Kale[a] & Mohinder Pal[b]

[a]*Department of Chemical Technology, University of Bombay, Matunga, 400 019 Bombay, India*
[b]*National Botanical Research Institute, Lucknow, India*

(Received 8 November 1995; revised version received 31 January 1996; accepted 31 January 1996)

Starches from newer food sources such as *Amaranthus paniculatas* and *Chenopodium quinoa* were studied for their possible role as biodegradable fillers in low density polyethylene (LDPE) films. Such starches have a unique feature of having an extremely small granule size (< 1 micron), which helps in better dispersion in polymeric films. In countries, where polymers are expensive, these starches could be used as inexpensive fillers. The effect of incorporating 3–15% corn starch, *Amaranthus paniculatas* and *Chenopodium quinoa* starch on the mechanical properties of the LDPE films was evaluated. The torque for blending of starches and LDPE was in general lower than that for LDPE alone. Incorporation of all the three starches decreased the tensile strength. Maximum decrease was observed with corn starch, and minimum decrease with *Chenopodium quinoa* and *Amaranthus paniculatas* was in between. Copyright © 1996 Elsevier Science Ltd

INTRODUCTION

Grain amaranths have been identified as promising food and feed source (Singhal & Kulkarni, 1988). It has about 12–18% lysine rich protein, and 5–8% fat that contains a relatively high level of squalene (Myers & Fox, 1994). The main constituent is however, 48–62% starch (Uriyapongson & Rayas-Duarte, 1994), concentrated in the perisperm (Zhao & Whistler, 1994a), which has been projected to have many food and non-food applications (Breene, 1991; Zhao & Whistler, 1994b).

Chenopodium quinoa has been recently identified to have promising potential in overcoming the world's food shortage. Its lysine-rich high protein grains (Gonsalez *et al.*, 1989; Dini *et al.*, 1992; Ruales & Nair, 1992; Ranhotra *et al.*, 1993), coupled with a desirable fatty acid composition (Przybylski *et al.*, 1994; Ruales & Nair, 1993) and high calcium and phosphorus contents (National Research Council, 1989) make it a unique food source. An added advantage is the nutritional quality of vegetable chenopods (Weber, 1978; Prakash *et al.*, 1993). The presence of bitter saponins, located primarily in the outer layer of the seed prevented it from attaining global importance (Reichert *et al.*, 1986; Muzui *et al.*, 1988; Ridout *et al.*, 1991).

The main constituent of *Chenopodium* (Lorenz, 1990) and *Amaranthus* (Singhal & Kulkarni, 1988) is the small granule sized (< 1 micron) starch. The fact that *Chenopodium* starch can be isolated in saponin-free form also qualifies it in food applications. Its industrial potential, however, remains untapped.

Starch blends with polyethylene have been used for the manufacture of biodegradable mulch films (Otey *et al.*, 1974, 1977). Starch at 7–10% level has been used commercially in England to produce 'biodegradable' polyethylene bags. The effect of modification of the starch to impart increased hydrophobicity was studied by Limaye (1993). Abundant literature exists on the use of starch and polyolefinic blends for various applications (Gonsalves *et al.*, 1991; Evangeliista, 1991; Knight, 1990; Ochi & Kuwaki, 1991; Fanta *et al.*, 1990; Breant, 1989). A loading of up to 10 parts per hundred (ppr) does not change the mechanical and thermal properties of the polymers appreciably. Above 10ppr, however, the composites are reported to become more susceptible to biological and oxidative attack, and also adversely affect mechanical properties (Griffin, 1974). Koch & Roper (1988) have observed better printability, improved water vapour permeability and improvement in mechanical properties on incorporation of untreated maize starch in polyethylene.

Starches more commonly reported for use as biodegradable fillers are from corn, tapioca, wheat or potato, which already have a well established demand in industries such as food, pharmaceuticals, textiles, cosmetics, etc. The average grain size of all these starches is more than one micron. Starch being hydrophilic, is not compatible with hydrophobic polymers. Smaller grain size, however, can be helpful in easy dispersion and hence at a given loading it may yield better properties. The present work compares the effect of incorporation of corn, *Chenopodium*, and *Amaranthus* starches on the mechanical properties of LDPE films. The latter two starches which have a very small grain size could serve as an alternative to rice starch, which has been known to give better dispersion, a property attributed to its small granule size.

MATERIALS AND METHODS

Corn starch was obtained from M/S Laxmi Starch, Mazgoan, Bombay. *Amaranthus paniculatas* grains were procured from a local market in Bombay city. *Chenopodium* grain was obtained from National Botanical Research Institute, Lucknow. Starches were isolated from *Amaranthus* and *Chenopodium* grains by the alkali steeping method (Yanez & Walker, 1986). The LDPE used was a commercial sample (FS-300) obtained from IPCL, Baroda. The following experiments were carried out:

(1) Blending of LDPE and starches: To a total weight of 45g, all three starches (dried at 55°C) under study, namely corn, *Amaranthus* and *Chenopodium* were individually incorporated in LDPE at levels of 3, 6, 9, 12, 15 and 20% w/w. The starch and the polymer were mixed thoroughly in a Haake Rheomix for 10 min at 20 rpm and at a melt temperature of 170°C. The torque generated during this process was noted.

(2) Preparation of sheets from blends of LDPE and starches: Samples of LDPE and starches mixed as above were used to prepare thin sheets of 0.5 mm thickness using a compression mould. The temperature and pressure conditions were 170°C and 100 kg/cm^2, respectively.

(3) Evaluation of mechanical strength of sheets prepared from blending of LDPE and starches: This was done as per the procedure reported by Brown (1988). Dumbell shaped test specimens as per ASTM were cut and analyzed for tensile strength and elongation at break using R&D Electronics Computerised Tensile Tester, and the following correlation:

$$\text{Tensile strength (N/m}^2) = \frac{\text{Tensile load}}{\text{Initial cross-sectional area}}$$

$$\text{Elongation at break (\%)} = \frac{l_f - l_0}{l_0} \times 100$$

where l_0 = initial length (cm) and l_f = final length (cm).

(4) Growth of micro-organisms on the films of LDPE filled with starches: The polymer sheets (containing 9% starch) were dipped in a 250 ml glass bottle containing 100 ml of 1% commercial glucoamylase in distilled water. The closed bottles were kept at room temperature for a period of 60 days and observed visually.

RESULTS AND DISCUSSION

Table 1 gives the torque generated during mixing of LDPE and starches under study. The torque for blending of LDPE and starches was, in general, lower than that for blending LDPE alone. For corn starch, no stable torque was observed, as was evident from wide fluctuations. Hence these values were not recorded. These fluctuations could be due to inadequate drying of starch. Amongst *Amaranthus* and *Chenopodium* starches, the torque for *Chenopodium* starch was lower. The torque was not affected by the level of starch blending in LDPE and remained constant up to 20% level used in the present study. A lower value of torque obtained on blending starches with LDPE suggests a decrease in apparent melt viscosity. It can therefore be stated that the decrease in melt viscosity is greater with *Chenopodium* starch as compared to *Amaranth* starch.

The reduction in viscosity may be due to formation of a double shell (inner one with higher density and outer one being loose) around the filler particle as explained by Malkin (1990). Thus initially, the viscosity decreases progressively with increase in concentration of filler. At some point, when 'crowding' begins, the viscosity increases rapidly with filler content due to increased drag.

Visually, the dispersion of starch appeared to be better and more uniform for small sized *Chenopodium* and *Amaranthus* starch as compared to corn starch.

Table 2 gives the mechanical properties of different samples. The tensile strength and percentage elongation both decreased for all types of starch fillers. However,

Table 1. Torque generated during mixing of LDPE and starch

Batch	Starch (%)	Torque (N·m)
LDPE	—	11.76
LDPE + *Amaranthus* starch		
	3	9.4
	6	9.4
	9	9.4
	12	9.4
	15	9.4
LDPE + *Chenopodium* starch		
	3	7.84
	6	7.84
	9	7.84
	12	7.84
	15	7.84

Table 2. Effect of incorporation of corn, *Amaranthus* and *Chenopodium* starches at 3–15% level on the mechanical properties of LDPE films[a,b,c,d,e]

Batch	Starch (%)	% Elongation at peak	% Elongation at break	Tensile strength (kg/cm^2)
LDPE	Nil	604	613.9	205.26
Corn starch				
	3	553.4	556.8	190.89
	9	377.1	381.4	116.32
	12	236.2	249.7	100.08
	15	418.7	430.9	136.41
Chenopodium starch				
	3	442.0	450.2	159.63
	6	378.1	388.9	135.68
	9	343.4	355.4	138.56
	12	287.6	299.5	107.35
	15	190.4	255.7	105.03
Amaranthus starch				
	3	504.3	514.1	177.61
	6	416.8	433.0	143.84
	9	403.7	413.2	142.20
	12	380.7	389.6	141.78
	15	324.3	336.5	128.90

[a]All tests were performed at 25±2°C and 65±2% RH.
[b]Each value is an average of four samples.
[c]Strain rate was 50mm/min.
[d]Load was 50kg.
[e]Sample length was 3.5cm.

the decrease is more significant for corn starch. *Amaranthus* starch has shown much better properties at a given loading. Also the decrease in tensile strength is much less over the range studied. The mechanical properties for *Chenopodium* and *Amaranthus* starches were better than those for corn starch as a filler. These two starches have an extremely small granule size of about 1 micron which may have aided proper dispersion of the starch and hence the observed trend. Even amongst *Amaranthus* and *Chenopodium* starches at the same level of incorporation, better results were obtained with waxy *Amaranthus* starch, which may be because of the extensive branched structure of amylopectin.

For certain applications such as inexpensive wrapping material or wrapping tape, this decrease in tensile strength may not be critical, but there are other applications such as carrier bags, where tensile strength assumes greater importance.

At the end of 60 days, the prominently visible microflora growth occurred on each of the three sheets. This clearly shows that growth of micro-organisms on all the three types of starch was possible and the growth rates were comparable, indicating no appreciable difference among corn, *Amaranth* and *Chenopodium* starch with respect to attack by microbes.

In developing countries, where starch is cheaper as compared to synthetic polymers, the role of starch as a filler is more attractive than its biodegradability. This application suggests that commercial exploitation of minor grains such as *Amaranthus* and *Chenopodium*, can be directed towards non-edible purposes. This may restrict or even prevent edible starches from being used as fillers in polymers.

CONCLUSIONS

Chenopodium and *Amaranthus* starch which do not have as-yet any edible applications and which have a very fine grain size can be used as biodegradable fillers in LDPE, in a similar way to corn starch. The mechanical properties of LDPE films filled with *Amaranthus* starch are better than those with corn starch at a given loading.

REFERENCES

Breant, P. (1989). Polyolefin composition for biodegradable films. Fr. Demande, 2,632,314. (Cited from *Chemical Abstract*, **113**, 153769j.).

Breene, W.M. (1991). Food uses of grain amaranth. *Cereal Foods World*, **36**, 426.

Brown, R. P. (1988). *Handbook of Plastics Test Methods*, 3rd edn. Longmann Scientific, London, p. 122.

Dini, N., Rastrrlli, L., Saturnino, P. & Schettino, O. (1992). A compositional study of *Chenopodium quinoa* seeds. *Nahrung*, **36**, 400.

Evangeliista, R. (1991). Effect of compounding and starch modification on properties of starch filled low density polyethylene. *Ind. Eng. Chem. Res.*, **30**, 1841.

Fanta, G.F., Swanson, C.L. & Doane, W.M. (1990). Composites of starch and poly(ethylene-coacrylic acid). *J. Appl. Polym. Sci.*, **40**, 811.

Gonsalez, J.A., Roldan, A., Gallardo, M., Escudero, T. & Prado, F.E. (1989). Quantitative determination of chemical compounds with nutritional value from Inca crops. *Plant Food Human Nutrition*, **39**, 331.

Gonsalves, K.E., Patel, S.H. & Chen, X. (1991). Development of potentially degradable materials for marine applications. *J. Appl. Polym. Sci.*, **43**, 405.

Griffin, G.J.L. (1974). Biodegradable fillers in thermoplastics. *Adv. Chem. Ser.*, **159**.

Knight, A.T. (1990). Starch derived shaped articles. PCT Int. Appl. WO 90,14,938. (Cited from *Chemical Abstract*, **114**, 230959w.).

Koch, H. & Roper, H. (1988). New industrial products from starch. *Starke*, **40**, 121.

Limaye, R. (1993). PhD Thesis, submitted to the University of Bombay.

Lorenz, K. (1990). Quinoa (*Chenopodium quinoa*) starch—physicochemical properties and functional characteristics. *Starke*, **42**, 81.

Malkin, A.Y. (1990). Filled Polymers I, Science and Technology. In *Advances in Polymer Science Vol. 96*. Springer-Verlag, Heidelberg, p. 69.

Muzui, F., Kasai, R., Ohtani, K. & Tanaka, O. (1988). Saponins from brans of quinoa. *Chem. Pharm. Bull.*, **36**, 1270.

Myers, D.J. & Fox, S.R. (1994). Alkali wet-milling characteristics of pearled and unpearled amaranth seed. *Cereal Chem.*, **71**, 96.

National Research Council (1989). *Recommended Dietary Allowances*, X edn. National Academic Press, Washington, DC.

Ochi, Y. & Kuwaki, T. (1991). Biodegradable polyolefin porous films. Jpn. Kokai Tokkyo Koho JP 03,100,028. (Cited from *Chemical Abstract*, **115**, 94121h.).

Otey, F.H., Mark, A.M., Mehtretter, C.L. & Russel, C.R. (1974). Starch based filling for degradable agricultural mulch. *Ind. Eng. Chem. Prod. Res. Develop.*, **13**, 90.

Otey, F.H., Westhof, R.P. & Russel, C.R. (1977). Biodegradable fillings from starch and ethylene acrylic acid copolymer. *Ind. Eng. Chem. Prod. Res. Develop.*, **16**, 305.

Prakash, D., Nath, P. & Pal, M. (1993). Composition variation of nutritional content of leaves, seed protein, fat and fatty acid profile of *Chenopodium* species. *J. Sci. Food Agric.*, **62**, 203.

Przybylski, R., Chauhan, G.S. & Eskin, N.A.M. (1994). Characterization of quinoa (*Chenopodium quinoa*) lipids. *Food Chem.*, **51**, 187.

Ranhotra, G.S., Gelroth, J.A., Glasser, B.K., Lorenz, K.J. & John, D.L. (1993). Composition and nutritional quality of quinoa. *Cereal Chem.*, **70**, 303.

Reichert, R.D., Tatarynovich, J.T. & Tyler, R.T. (1986). Abrasive dehulling of quinoa (*Chenopodium quinoa*). Effect on saponin content as determined by an adapted hemolytic assay. *Cereal Chem.*, **63**, 471.

Ridout, C.L., Price, K.R., Dupont, M.S., Parker, M.L. & Fenwick, G.R. (1991). Quinoa saponins—analysis and preliminary investigations into effects of reduction by processing. *J. Sci. Food Agric.*, **54**, 165.

Ruales, J. & Nair, B.M. (1992). Nutritional quality of the protein in quinoa seeds. *Plant Foods Human Nutrition*, **42**, 1.

Ruales, J. & Nair, B.M. (1993). Contents of fat, vitamins and minerals in *C. quinoa* seeds. *Food Chem.*, **48**, 131.

Singhal, R.S. & Kulkarni, P.R. (1988). Amaranths—an underutilized resource. *Int. J. Food Sci. Technol.*, **23**, 125.

Uriyapongson, J. & Rayas-Duarte, P. (1994). Comparison of yield and properties of amaranth starches using wet and dry–wet milling processes. *Cereal Chem.*, **71**, 571.

Weber, E.J. (1978). The Inca's ancient answer to food shortage. *Nature*, **272**, 486.

Yanez, G.A. & Walker, C.E. (1986). Effect of tempering parameters on extraction and ash of proso milled flours and partial characterization of proso starch. *Cereal Chem.*, **63**, 164.

Zhao, J. & Whistler, R.L. (1994a). Isolation and characterization of starch from amaranth flour. *Cereal Chem.*, **71**, 392.

Zhao, J. & Whistler, R.L. (1994b). Spherical aggregates of starch granules as flavour carriers. *Food Technol.*, **48**(7), 104.