Available online at www.sciencedirect.com
SCIENCE @ DIRECT®

Carbohydrate Polymers 53 (2003) 95–99

Carbohydrate Polymers
www.elsevier.com/locate/carbpol

Thermoplastic starch/natural rubber blends

A.J.F. Carvalho[a], A.E. Job[b], N. Alves[b], A.A.S. Curvelo[a], A. Gandini[c,*]

[a]*Instituto de Química de São Carlos, Universidade de São Paulo, CP 780, 13.560-970 São Carlos, SP, Brazil*
[b]*Departamento de Física, Química e Biologia, FCT-UNESP, CP 467, 19060-900 Presidente Prudente, SP, Brazil*
[c]*École Française de Papeterie et des Industries Graphiques (INPG), BP 65, 38402 St Martin d'Hères, France*

Received 11 October 2002; revised 14 October 2002; accepted 18 December 2002

Abstract

Thermoplastic starch/natural rubber polymer blends were prepared using directly natural latex and cornstarch. The blends were prepared in an intensive batch mixer at 150 °C, with natural rubber content varying from 2.5 to 20%. The blends were characterised by mechanical analysis (stress-strain) and by scanning electron microscopy. The results revealed a reduction in the modulus and in tensile strength, becoming the blends less brittle than thermoplastic starch alone. Phase separation was observed in some compositions and was dependent on rubber and on plasticiser content (glycerol). Increasing plasticiser content made possible the addition of higher amounts of rubber. The addition of rubber was, however, limited by phase separation the appearance of which depended on the glycerol content. Scanning electron microscopy showed a good dispersion of the natural rubber in the continuos phase of thermoplastic starch matrix.

Keywords: Starch; Natural rubber; Biodegradable blends

1. Introduction

The development of plastics using renewable resources which are naturally biodegradable and the possibility of combining their biodegradability with cost reduction and market needs have been the object of intensive academic and industrial research. Starch is one of the main natural polymers studied for the production of biodegradable materials (Avérous, Frigant, & Moro, 2001; Bastioli, 1995; Carvalho, Curvelo, & Agnelli, 2002; Curvelo, Carvalho, & Agnelli, 2002; Dufresne & Vignon, 1998; Griffin, 1977, 1978; Otey & Westhoff, 1979, 1982; Röper & Koch, 1990; Shogren, Fanta, & Doane, 1993; Willett, Jasberg, & Swanson, 1994), since it is one of the major components of cereal grains and tubers already widely used in the food, paper and textile industries. Starch is composed of amylose and amylopectin, which are both polysaccharides made up of α-D-glucopyranosyl units linked by (1–4) and (1–6) linkages (Kainuma, 1984). This natural macromolecular combination, either as a pure substance, or in its naturally occurring granular form, cannot be processed as a thermoplastic material because it decomposes before melting. Several processing alternatives have therefore been envisaged.

The first attempts to obtain starch-based materials involved the utilisation of starch granules as fillers for synthetic polymers, such as poly(ethylene) and poly(propylene) (Griffin, 1977, 1978), and destructured or disrupted starch granules in blends with synthetic polymers (Otey & Westhoff, 1979, 1982). More recently, starch has been used as the main polymer in macromolecular compositions which can be processed as thermoplastics such as poly(ethylene), poly (vinyl chloride), etc. In this case, the granular structure of starch is completely disrupted by the use of plasticisers under heating, giving rise to a continuous phase in the form of a viscous melt which can be processed following conventional plastic processing techniques such as injection moulding or extrusion. These types of starch compositions are commonly known as thermoplastic starches (TPS) (Röper & Koch, 1990; Shogren et al., 1993). Unfortunately, TPS present some drawbacks, such as low degradation temperatures, which make them difficult to process, poor mechanical properties and high water susceptibility. Much work has been carried out to overcome these drawbacks,

---

[*] Corresponding author. Tel.: +0033-4-76-82-69-00; fax: +0033-4-76-82-69-33.
E-mail address: alessandro.gandini@efpg.inpg.fr (A. Gandini).

0144-8617/03/$ - see front matter © 2003 Elsevier Science Ltd. All rights reserved.
doi:10.1016/S0144-8617(03)00005-5

including the use of reinforcements (Avérous et al., 2001; Carvalho et al., 2002; Curvelo et al., 2002; Funke, Bergthaller, & Lindhauer, 1998; Wollerdorfer & Bader, 1998) and the combination of TPS with other polymers (Arvanitoyannis, Kolokuris, Nakayama, & Aiba, 1997; Averous, Moro, Dole, & Frigant, 2000; Griffin, 1994; St-Pierre, Favis, Ramsay, Ramsay, & Verhoogt, 1997; Yang, Bhattacharya, & Vaidya, 1996). A few studies dealing with the use of rubber in these polymer blends are described in the literature (Arvanitoyannis et al., 1997; Yang et al., 1996). Thus, solid *trans*-1,4-poly (isoprene) (gutta percha) has been added to starch in the presence of compatibilisers, such as an ethylene–acrylic acid copolymer (Arvanitoyannis et al., 1997).

The aim of this work is the preparation of blends of thermoplastic starch using directly the latex of *Hevea Brasiliensis*, without the use of 'external compatibilisers'. Natural rubber (NR), *cis*-1,4-poly(isoprene), occurs in several plant species, but its most important source is the *Hevea Brasiliensis* tree, which accounts for over 99% of the world's natural rubber production. Natural rubber is extracted as a latex or 'milk', viz. an aqueous emulsion or dispersion of the natural polymer (~96 wt% of solids) and other substances, such as proteins (~1%), lipids (~3%) and traces of potassium, magnesium, and copper (Greve, 1993). An adsorbed layer of protein and phospholipids stabilises the rubber particles.

2. Experimental

2.1. Materials

Starch was kindly supplied by Corn Products do Brasil and was a conventional cornstarch containing 28% of amylose. The natural rubber latex was used directly as extracted from the trees (*Hevea Brasiliensis*) and was stabilised by adding 2.5% of a 28% ammonium hydroxide solution. Its solid contents (or non-volatile components) amounted to 35 wt%, as determined by drying the emulsion in an oven at 110 °C for 12 h. Glycerol was a commercial reagent grade compound, used without any further treatment.

2.2. Preparation of the thermoplastic starch/natural rubber blends (TPS/NR)

The blends were prepared with a glycerol-to-starch proportion varying from 20 to 50% and a quantity of dry rubber to TPS in the range of 2.5–20% with respect to total weight. Starch, glycerol and latex were hand mixed in a beaker until a homogeneous mixture was obtained. The compositions with a high proportion of latex + glycerol, gave rise to a paste-like mass. These mixtures were directly processed in a Haake Rheomix 600 intensive batch mixer equipped with roller rotors and operated at 150 °C and 50 rpm for 6 min. The ensuing materials were hot pressed at 150–160 °C into 10 by 10 cm plates 2.5 mm thick.

2.3. Mechanical tests

The plates were cut into dumb-bell shaped specimens for stress–strain tests, which were performed with a model 5500 R Instron testing machine, operated at 50 mm/min. These tests provided the ultimate tensile strength (UTS), the secant elastic modulus at 1% strain ($E_{1\%}$) and the strain at break (ε_r). Five specimens were tested for each composition, after a four-week period of conditioning at 25 °C and 53% relative humidity (RH). The specimen shapes and the operating conditions were in accordance with the ASTM D 638M standard.

2.4. Scanning electron microscopy (SEM)

Fragile fractured surfaces of the blend samples cooled in liquid nitrogen, were studied with a model DSM 960 Zeiss Digital Scanning Microscope, equipped with a tungsten filament operated at 10–15 kV. The samples were vacuum coated with a 200 Å layer of gold.

3. Results and discussion

The results related to modulus ($E_{1\%}$), elongation (ε_r) and ultimate tensile strength (UTS) are presented in Table 1.

The addition of small amounts of rubber to the starch blends containing 20% of glycerol (TPS/NR-1 and TPS/NR-2) induced their softening, as shown by the corresponding decrease in modulus. Indeed a considerable modulus drop already occurred with the TPS/NR-1 sample, which only contained 2.5% of rubber. A subsequent rubber addition to 5.0%, produced a less pronounced decrease in modulus. The tensile strength followed the same trend for these samples, whereas the elongation at break showed modest and irregular variations. A further increase in rubber contents, namely 10 and 20% (TPS/NR-3 and TPS/NR-4) produced a visible phase separation and the blends became brittle with an irregular aspect with regions bearing free rubber. The mechanical properties of these materials showed a high dispersion of data points (see Table 1) because of their heterogeneous character.

For the blends with 30% glycerol and rubber contents up to 10%, the modulus variations were modest, probably because the parent TPS had an intrinsically low modulus, whereas the tensile strength decreased more substantially with the addition of rubber. For the highest rubber content, TPS/NR-8, both the modulus and the tensile strength decreased dramatically. Whereas samples TPS/NR-5, TPS/NR-6 and TPS/NR-7 were transparent, TPS/NR-8 was opaque, indicating some phase separation. The values of the elongation at break for these blends showed a small and irregular decrease with increasing rubber content.

Table 1
Values of modulus ($E_{1\%}$), elongation (ϵ_r) and ultimate tensile strength (UTS) determined for the blends conditioned at 53% relative humidity. All percentages are by weight: that of glycerol refers to starch, whereas that of rubber refers to the total weight

Composition	Glycerol content (%)	Rubber content (%)	$E_{1\%}$(Mpa)[a]	UTS(MPa)[a]	ε_r (%)[a]
GLI-20	20	0	466(25)	9.0(1)	22(4)
TPS/NR-1	20	2.5	231(16)	6.5(1)	30(8)
TPS/NR-2	20	5	183(14)	4.2(1)	19(10)
TPS/NR-3[b]	20	10	47(40)	0.9(1)	5(6)
TPS/NR-4[b]	20	20	67(64)	0.9(1)	16(20)
GLI-30	30	0	63(6)	4(0.2)	52(9)
TPS/NR-5	30	2.5	66(8)	3(0.5)	27(6)
TPS/NR-6	30	5	61(8)	2(0.5)	10(5)
TPS/NR-7	30	10	55(3)	2.4(0.4)	15(4)
TPS/NR-8[b]	30	20	6(4)	0.7(0.1)	19(3)
GLI-40	40	0	19(9)	2(0.1)	29(6)
TPS/NR-9	40	2.5	14(7)	1.4(0.1)	17(2)
TPS/NR-10	40	5	21(7)	1.7(0.1)	24(2)
TPS/NR-11	40	10	17(7)	1.6(0.1)	26(4)
TPS/NR-12	40	20	20(3)	1.4(0.1)	23(3)

[a] Number in parenthesis after the values are standard deviations.

[b] Brittle samples with visible phase separation.

For the blends containing 40% of glycerol, the effect of rubber addition on modulus, tensile strength and elongation was modest, again because the mechanical properties of the starting TPSs were at their lowest level.

These results showed that the addition of rubber to starch–glycerol blends is limited by phase separation that seems to be dependent on the glycerol content in the sense that as the latter was increased, the phase separation

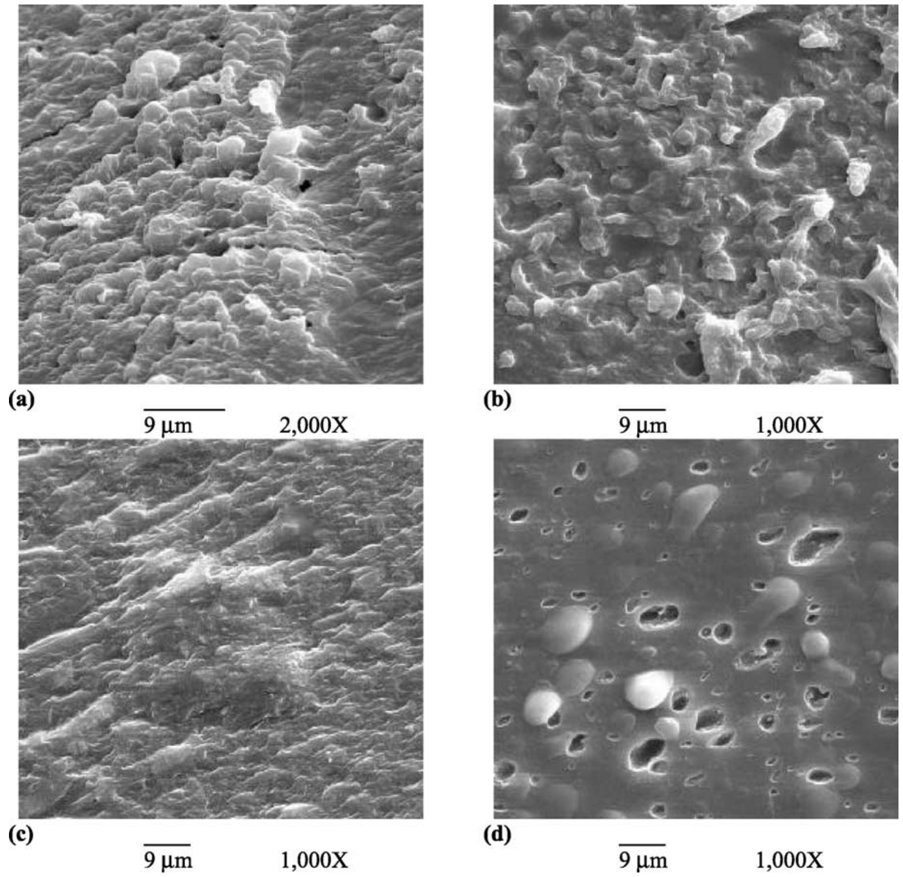

Fig. 1. Scanning electron micrographs of fragile fractures (liquid nitrogen) of starch/natural rubber blends, (a) TPS/NR2, (b) TPS/NR8, (c) TPS/NR10 and (d) TPS/NR12.

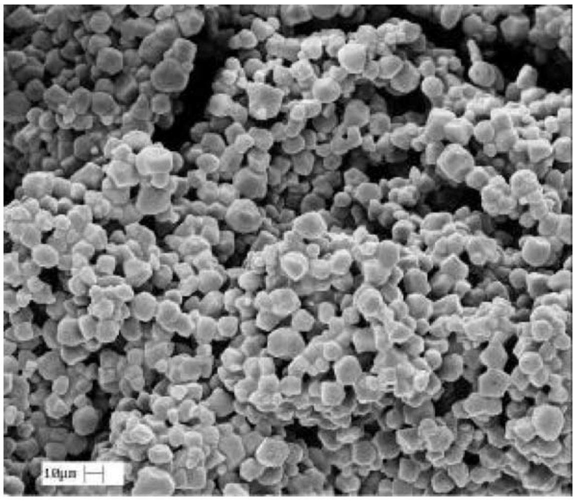

Fig. 2. Scanning electron micrograph of cornstarch granules at 1000 × magnification.

occurred at higher rubber contents. It appears therefore that glycerol played the role of both starch plasticiser and starch–rubber compatibiliser.

Fig. 1 shows three typical SEM images of blends, displaying the dispersed phase of rubber as particles homogeneously distributed in the TPS matrix.

Despite the fact that the contrast between starch and rubber was poor, it was possible to identify the two distinct phases. The dispersed rubber particles appeared as regular spheres with diameters varying between 2 and 8 μm. The adhesion between phases for the composites with 20, 30 and 40% glycerol and 5% rubber seemed to be good, since no voids of removed rubber were visible, as shown in Fig. 1(a)–(c). In Fig. 1(d), corresponding to the blend with 40% glycerol and 20% rubber, some voids and round rubber particles were visible, suggesting a poorer adhesion between the components of the blend.

The mixing process plays an important role in the morphology of these blends and, considering the fact that the batch mixer operated at low shear, the dispersion of rubber in the starch matrix was quite satisfactory. The quality of these dispersions was a consequence of the utilisation of the latex instead of solid rubber. In fact, the average particle size of latex is between 0.15 and 3.0 μm (Greve, 1993) and some of the rubber spheres visible in the SEM images of the corresponding blends reflected the presence of those individual original latex particles. The largest rubber domains were probably generated by the agglomeration of those elementary particles. Since the starch used in this study also presented a granular morphology, with an average size of 10 μm (see Fig. 2), its particles could have been confused with the rubber ones. However, the shape of the starch grains was polygonal, as shown in Fig. 2, so that a distinction based on shape could be made when inspecting the SEM images. It was therefore concluded that the continuous phase was made up of plasticised starch and the microspheres belonged to the elatomeric phase.

Fig. 3 shows the SEM micrographs of the fractured frozen samples, in which it was possible to visualise what we believe to be rubber particles stretched between two regions. Additionally, our extensive experimentation with thermoplastic starch granules without rubber (Curvelo et al., 2002, Carvalho et al., 2002), in conditions similar to those employed in this work, generated fragile cold fractures with flat surfaces without any evidence of residual granular structure.

As it was pointed earlier, the adhesion between the blend components seemed to be good. This interfacial quality can be attributed to the presence of proteins and lipids at the surface of the rubber particles in the latex acting as a compatibiliser between starch, a polar matrix, and rubber, a non-polar material. The direct use of the natural latex is therefore especially interesting in this context because its non-rubber constituents do not need to be removed since they play a positive role as blending agents.

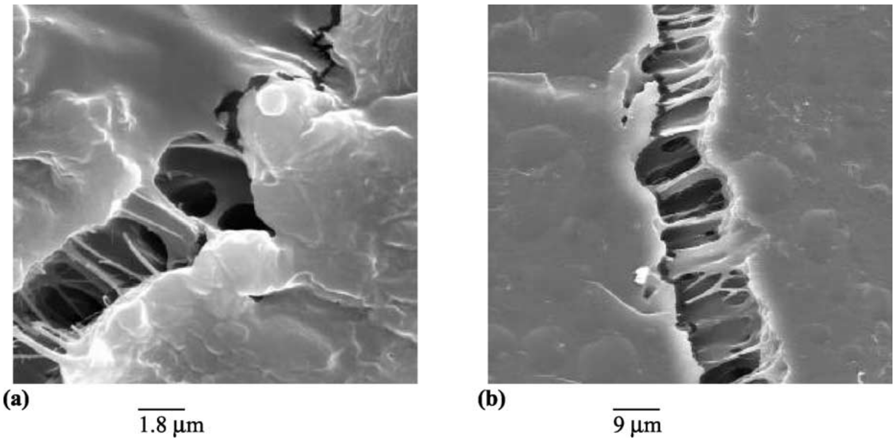

Fig. 3. Scanning electron micrograph of fractured TPS/NR blends showing the stretch of rubber particles, (a) TPS/NR-2 and (b) TPS/NR-3, at 5000 × and 1000 × magnification, respectively.

4. Conclusions

Blends of thermoplastic starch and natural rubber were obtained directly form the latex and granular cornstarch. The dispersion of rubber in the thermoplastic starch matrix was homogeneous thanks to the presence of the aqueous medium, with rubber particles ranging in size from 2 to 8 μm. The process employed in this investigation called upon the use of both starch and latex in their natural form, without any kind of purification. Moreover, the presence of the non-rubber constituents of the latex was responsible, not only for insuring the latex stability, but also for improving the compatibility between the thermoplastic starch and the natural rubber phases. The addition of rubber was, however, limited by phase separation the appearance of which depended on the glycerol content. Finally, glycerol seemed to contribute to both the platicisation of starch and to the improvement of the starch–rubber interface.

Acknowledgements

We are grateful to FAPESP and COFECUB for financial support and to Corn Products do Brasil for a generous gift of cornstarch.

References

Arvanitoyannis, I., Kolokuris, I., Nakayama, A., & Aiba, S. (1997). Preparation and study of novel biodegradable blends based on gelatinized starch and 1,4-transpolyisoprene (gutta percha) for food packaging or biomedical applications. *Carbohydrate Polymers*, *34*, 291–302.

Avérous, L., Frigant, C., & Moro, L. (2001). Plasticized starch cellulose interactions in polysaccharide composites. *Polymer*, *42*, 6565–6572.

Avérous, L., Moro, L., Dole, P., & Frigant, C. (2000). Properties of thermoplastic blends: Starch-polycaprolactone. *Polymer*, *41*, 4157–4167.

Bastioli, C. (1995). Starch polymer composites em degradable polymers. In G. Scott, & D. Filead (Eds.), *Degradable polymers* (pp. 112–137). Cambridge, UK: Chapman Hall.

Carvalho, A. J. F., Curvelo, A. A. S., & Agnelli, J. A. M. (2002). Wood pulp reinforced thermoplastic starch composites. *International Journal of Polymeric Materials*, *51*, 647–660.

Curvelo, A. A. S., Carvalho, A. J. F., & Agnelli, J. A. M. (2002). Thermoplastic starch-cellulosic fibers composites: Preliminary results. *Carbohydrate Polymers*, *45*, 183–188.

Dufresne, A., & Vignon, M. R. (1998). Improvement of starch film performances using cellulose microfibrils. *Macromolecules*, *31*, 2693–2696.

Funke, U., Bergthaller, W., & Lindhauer, M. G. (1998). Processing and characterization of biodegradable product based on starch. *Polymer Degradation and Stability*, *59*, 293–296.

Greve, H. H. (1993). Natural rubber. In B. Elvers, S. Hawkins & G. Schultz (Eds.), (5th ed.) (*Vol. A23*) (pp. 225*Ullmann's encyclopedia of industrial chemistry*, Weinheim: VCH.

Griffin, G. J. L (1977). US Patent, 4,021,388.

Griffin, G. J. L (1978). US Patent, 4,125,495.

Griffin, G. J. L. (1994). Starch polymer blends. *Polymer Degradation and Stability*, *45*, 241–247.

Kainuma, K. (1984). Starch oligosaccharides: Linear, branched and cyclic. In R. L. Whistler, J. N. Bemiller, & E. F. Paschall (Eds.), *Starch: Chemistry and technology* (pp. 125–152). San Diego, CA: Academic Press.

Otey, F. H., Westhoff, R. P (1979). US Patent, 4,133,784.

Otey, F. H., Westhoff, R. P (1982). US Patent, 4,337,181.

Röper, H., & Koch, V. (1990). The role of starch in biodegradable thermoplastic materials. *Starch/Stärke*, *42*, 123–130.

Shogren, R. L., Fanta, G., & Doane, W. M. (1993). Development of starch based plastics—A reexamination of selected polymer systems in historical perspective. *Starch/Stärke*, *45*, 276–280.

St-Pierre, N., Favis, B. D., Ramsay, B. A., Ramsay, J. A., & Verhoogt, H. (1997). Processing and characterization of thermoplastic starch/polyethylene blends. *Polymer*, *38*, 647–655.

Willett, J. L., Jasberg, B. K., Swanson, L. L (1994). *Melt Rheology of Thermoplastic starch*. ACS Symposium Series 575. Polymers from Agricultural Coproducts, Chapter 3, pp. 50–68. American Chemical Society, Washington.

Wollerdorfer, M., & Bader, H. (1998). Influence of natural fibres on the mechanical properties of biodegradable polymers. *Industrial Crops and Products*, *8*, 105–112.

Yang, Z., Bhattacharya, M., & Vaidya, U. R. (1996). Properties of ternary blends of starch and maleated polymers of styrene and ethylene propylene rubber. *Polymer*, *37*, 2137–2450.