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Synthesis and properties of composites of starch and chemically modified natural rubber

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Abstract

A means is developed for forming polysaccharide-based composites with useful material properties through use of unmodified and chemically modified natural rubber latex (NRL). Starch was used as a model for polysaccharides. The NRL was modified by grafting with dimethylaminoethyl methacrylate (DMAEMA) to form a latex with cationic water-soluble polymeric ‘hairs’ of polyDMAEMA, which should form hydrogen bonds with starch. Starch solutions, containing 20% glycerol as a film-forming aid, and the modified NRL were mixed and films allowed to form. The unmodified latex acted only as filler in the starch films, but with modified NRL, the mechanical properties of the films were significantly altered. The elastic modulus was greatly decreased and strain at break greatly increased. The glass transition temperature increased from $-48\text{ }^{\circ}\text{C}$ to $-32\text{ }^{\circ}\text{C}$, suggesting significant compatibilization. Freeze-fracture TEM micrographs indicate strong interactions between the surface of the modified NRL and starch. The polyDMAEMA chains are more hydrophilic than the starch, and the addition of grafted latex results in a 20° drop of the water contact angle of the formed film, and a 25% increase of the water absorption compared to the native starch; with unmodified NRL, the opposite effect was observed.

Keywords: Starch; Natural rubber latex; Polymer colloid

1. Introduction

The use of polymers from renewable resources is an environmentally advantageous alternative to synthetic polymers in some applications. Many polysaccharide biopolymers have been examined in this context [1], with the long-term aim of value-adding to ‘waste’ agricultural byproducts such as sugarbeet pulp and rice husks. Pure starch is a good model for such biopolymers, and also is useful as a substrate in its own right.

The thermoplastic properties of starch have been extensively studied [2], and are directly related to its water content; in its dry state, the glass transition temperature (T_g) of starch is above its degradation temperature. While many technologies have been used to process starch, the easiest way of obtaining a film is by

casting from a solution. To obtain useful materials from starch, the native properties must be enhanced, because of starch’s high water sensitivity and poor mechanical properties compared to those of synthetic polymers. The influence of water content [3] and of external plasticizers like glycerol [4] and sorbitol [5] have been investigated to decrease the brittleness of these materials. Vegetable fibres [6] and mineral fillers [7,8] have been used to enhance the mechanical strength of the starch. Starch and related biopolymers have been chemically modified [9,10] or blended with synthetic polymers [11,12] to improve mechanical strength and water resistance.

As a suitable polymer for use in starch modification, natural rubber latex (NRL) has many attractions. It is a latex, which facilitates blending with a starch solution and indeed with any particulate substance such as sawdust or pulp; it is a renewable resource, can be biodegraded [13], and contains natural stabilizers (i.e. proteins and lipids) which should help compatibilization with starch. The polymer is essentially 100% *cis*-1,4-polyisoprene, and this

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conformation leads to a number of useful mechanical properties such as improved mechanical strength on stretching. It is also inexpensive. NRL is supplied as the natural latex (which has a broad particle size distribution, ranging from 100 nm to 2 μ m), stabilized with ammonia. The abbreviation NRL will always be used for this ‘high-ammonia’ latex.

Recently, a method has been developed to modify NRL by grafting a ‘hairy layer’ of hydrophilic polymers [14]. Of the various hydrophilic monomers which could be used for this purpose, that chosen here is dimethylaminoethyl methacrylate, DMAEMA. This grafting procedure has been shown by NMR [15] and colloidal stability studies [14,16] to yield covalently bonded polyDMAEMA hairs as well as some free polyDMAEMA in the water phase [16]. The amine functionality of polyDMAEMA confers considerably enhanced colloidal stability on NRL: while NRL coagulates when the pH is taken below \sim 8.5, the polyDMAEMA-modified NRL is stable to pH values as low as 2 [14]. DMAEMA is biodegradable, although has some ecotoxicity [17].

The aim of this work is to use NRL and NRL modified by polyDMAEMA directly in the wet casting of starch films and to investigate the effect on the properties of these films, with the long-term goal of value-adding to agricultural ‘waste’ byproducts. Alternative approaches on starch/rubber blends have examined the use of starch as a filler in a rubber matrix [18,19] with phase compatibilization by chemical modification of either the rubber [20–23] or the starch [24–26].

2. Materials and methods

2.1. Materials

Rice starch (chosen because this is an important product in Australia) was supplied by Sigma. Because it has been observed [18] that the amylose content of starch can affect mechanical properties in starch/rubber blends, the amylose content of this sample was measured as follows. Starch–iodine complexes were made for the starch following the standard method for quantifying amylose [27,28], and absorbance was measured every 1.25 nm over the visible spectrum using a scanning spectrophotometer (GBC UV/VIS 918). The amylose content was thus found to be 28%. The present data are for this fixed amylose content. NRL (‘high ammonia latex’, 61% solids) from RLA Polymers was used as supplied. Dimethylaminoethyl methacrylate (DMAEMA), cumene hydroperoxide (CHP), tetraethylenepentamine (TEPA), all Aldrich Reagent Grade, were used as received. Reagent grade glycerol and analytical grade $Mg(NO_3)_2$, K_2SO_4 , dimethyl sulfoxide (DMSO) and acetone were used as received.

2.2. Grafting procedure

To graft DMAEMA onto NRL, the following procedure was used, following that of Lamb et al. [14]. The weight of DMAEMA was chosen to be 5, 10 and 15% w/w with respect to dried weight of rubber in the NRL, these grafted rubber latexes being denoted GRL5, GRL10 and GRL15. NRL, DMAEMA, CHP, TEPA and 2.5% ammonia solution were combined in the amounts given in Table 1. The reaction mixture was agitated with a low-shear impeller, a 10% aqueous solution of TEPA was then added shot-wise over 1 h at 5 min intervals, and the system was cooled in an ice/water bath during the first 8 h of reaction before gradually warming to room temperature, and allowed to continue react for another 16 h. After reaction, the latex was filtered through glass wool and neutralized to pH 7 with 1 M hydrochloric acid solution. The resulting latex as used in the present paper contains both grafted and ungrafted polyDMAEMA [16]. For reasons detailed elsewhere [16], the amount of grafting is extremely hard to quantify, because of the difficulty of quantitatively removing all ungrafted polyDMAEMA. However, NMR studies on the gel fraction [15], which will contain the lowest amount of grafted polymer [15], show that the lower bound for the amount of grafted polyDMAEMA in the present system is 5 mol%.

2.3. Film formation

Granular starch was dispersed in ultra-pure water (3% w/w) and gelatinized by stirring and heating to 75 $^{\circ}$ C followed by dissolution in an autoclave at 120 $^{\circ}$ C under 120 kPa pressure for 30 min. A clear, viscous solution was obtained. To this solution, glycerol (as plasticizer for the starch), 20% w/w relative to starch on a dry basis, was added. Starch/latex samples with ratios of 100/0, 95/05, 90/10, 85/15, 80/20 and 70/30 (w/w on a dry basis, that of the latex referring to the solid content obtained after drying at 60 $^{\circ}$ C) were made by adding latex to the starch/glycerol solution. The system was homogenized by vigorous shaking of the mixture. This was then poured on polystyrene dishes and allowed to dry at 25 $^{\circ}$ C over 3 days. The resulting films (20–50 μ m in thickness) were then dried at 60 $^{\circ}$ C overnight

Table 1
Recipes for grafted natural rubber latexes (GRL), final solid content, and amount of DMAEMA relative to the total mass of solids

	GRL5	GRL10	GRL15
NRL/g	51.85	52.07	51.96
DMAEMA/g	1.604	3.208	5.238
CHP/g	0.069	0.139	0.205
NH_3 (2.5%)/g	100.7	100.1	100.1
TEPA/g ^a	0.095	0.179	0.270
Solid content (%)	21.1	22.1	23.2
DMAEMA content (%)	3.0	5.8	9.1

^a Made up to 10% solution with distilled water.

and maintained at 54% relative humidity (r.h.) over a saturated solution of $\text{Mg}(\text{NO}_3)_2$ in a desiccator at room temperature.

2.4. Mechanical properties

Standardized dumbbell-shaped specimens (ISO 527-2) with a 13 mm long and 3.3 mm wide rectangular working section were cut from the films with a cutting die. These were then tested for tensile resistance on a TA Instrument DMA with a force ramp of 1 N min^{-1} . This gave ultimate tensile strength (UTS), elastic modulus (E) and the elongation at break (EL); the film toughness was obtained from the area of the stress–strain curves, and the tensile strength–elastic modulus ratio UTS/E also obtained [29]. Five to seven measurements were made for each type of film. Dynamic mechanical analyses (DMA) of the films were performed over the temperature range -120 to 20°C with a scanning rate of 3°C min^{-1} . The static force, amplitude and frequency were maintained constant at 0.2 N, $2 \mu\text{m}$ and 1 Hz, respectively. To avoid water condensation, all dumbbell specimens were covered with a layer of silicone grease, which does not affect the dynamic mechanical properties of starch-based materials [5].

2.5. Freeze fracture

In order to examine their internal structure, the films were freeze-fractured using the following procedure. A 1 mm thick cylinder of film was obtained by casting multiple layers of film-forming latex/starch mixtures between two copper cups. The cylinders were then frozen at -150°C and under reduced pressure before being fractured with a blade. The freeze-fractured surfaces were shadowed with platinum and then with carbon. The replicas were then isolated from the samples by washing in DMSO and acetone before being placed on a copper grid. Finally they were observed on a Philips CM120 TEM.

2.6. Contact angle with water

The films were kept at 54% r.h. before being tested on a Contact Angle Meter GBX (Romans sur Isère, France). Three drops of water were placed successively on a piece of each film, and their left and right angles measured. The value reported is the average of six measurements.

2.7. Water absorption

Pieces of film equilibrated at 54% r.h. were placed in a sealed container above a saturated solution of K_2SO_4 (97% r.h.) for 24 h. They were weighed at regular intervals; mass-gain values reported below are the average of three measurements.

3. Results and discussion

3.1. Mechanical properties

The properties arising from using unmodified NRL are first considered. As noted recently [30], adding NRL to starch-based materials without any external plasticizer does not result in any improvement of the material properties. It was found in the present work that it is, however, possible to add up to 20% of NRL without any apparent phase separation, this being presumably due to the natural stabilizers in NRL (proteins and phospholipids). With the further addition of 20% (w/w with respect to dry starch) of glycerol, one can add as much as 30% NRL without phase separation. This amount of glycerol acts as a plasticizer, and the formed films are supple enough to be easily handled, even without the addition of latex. Mechanical properties of the formed films are shown in Table 2. Addition of from 5 to 20% NRL caused a decrease of both tensile strength and elastic modulus but no modification of the elongation at break, of film toughness or of UTS/E (which quantifies the resistance of the films to crack [29]). Adding 30% NRL to the glycerol-plasticized starch films resulted in an improvement of the film plasticity: the tensile strain increased to 11% with no significant change in tensile strength or elastic modulus. The rubbery phase now appears to interact significantly with the starch matrix, rather than merely acting as an inert filler.

The effects of addition of modified (grafted) NRL are now examined. It is expected that the addition of modified natural rubber, with the hydrophilic hairs likely to form hydrogen bonds with the starch, would enhance compatibility between the hydrophobic component (polyisoprene), to which they are grafted, and the hydrophilic (starch) component. When considering the properties of the effects of addition of modified NRL, it is also necessary to consider which effects may arise from ungrafted polyDMAEMA alone.

The interpretation of the observations is made complex by the presence of both grafted and ungrafted polyDMAEMA. Unfortunately, it proved impossible to separate the free chains from the latex, presumably because the free chains tend to strongly associate with grafted polyDMAEMA on the particle surface. Attempted separation using centrifugation led on the one hand to an unrealistically low value of the fraction of unbound chains and moreover centrifugation resulted in irreversible coagulation of the latex. However, the total amount of free chains could never exceed 4.5% of the starch weight (for an addition of 30% of GRL15), and such a low ratio of external plasticizer is very unlikely to be responsible for the large change in properties observed.

This difficulty in principle could be overcome by adding free polyDMAEMA to NRL and carrying out the same tests. However, this leads to coagulation of the NRL if one adds

Table 2

Average value and standard deviation (in parentheses) of the ultimate tensile strength (UTS), strain at break (EL), elastic modulus (E), toughness and UTS/ E value of the different films conditioned at 54% relative humidity

	Latex content (% w/w)	Ultimate tensile strength UTS (MPa)	Strain at break (%)	Elastic modulus E (MPa)	Toughness (MJ m^{-3})	UTS/ E
Reference	0	12.3 (1.2)	4.0 (0.4)	46.0 (6.9)	0.33 (0.05)	0.27 (0.07)
NRL	5	10.3 (0.4)	4.1 (0.7)	33.1 (1.9)	0.26 (0.03)	0.31 (0.03)
	10	10.1 (0.8)	3.5 (0.7)	30.8 (3.5)	0.25 (0.02)	0.33 (0.06)
	15	8.4 (0.7)	4.4 (0.6)	27.1 (2.2)	0.26 (0.01)	0.31 (0.05)
	20	7.9 (0.9)	4.6 (0.4)	23.6 (3.6)	0.27 (0.01)	0.33 (0.11)
	30	8.0 (0.7)	11.0 (1.0)	19.5 (2.1)	0.7 (0.1)	0.41 (0.1)
GRL5(n)	5	9.8 (1.2)	4.2 (0.3)	31.6 (5.2)	0.28 (0.01)	0.31 (0.12)
	10	9.6 (1.4)	3.4 (1.1)	36.7 (5.9)	0.31 (0.06)	0.26 (0.1)
	15	8.6 (0.9)	5.9 (1.2)	21.5 (2.1)	0.32 (0.03)	0.4 (0.08)
	20	8.9 (0.9)	5.3 (0.7)	23.2 (0.8)	0.30 (0.06)	0.38 (0.06)
	30	6.4 (0.7)	12.2 (2.2)	15.6 (3.6)	0.58 (0.06)	0.41 (0.18)
GRL5	5	11.0 (0.3)	5.4 (0.4)	23.6 (2.4)	0.3 (0.1)	0.47 (0.06)
	10	9.6 (2.0)	6.8 (2.7)	19.6 (2.4)	0.3 (0.1)	0.49 (0.18)
	15	6.3 (0.9)	16.2 (6.2)	8.5 (2.5)	0.6 (0.2)	0.74 (0.46)
	20	4.8 (0.4)	20.4 (3.0)	5.8 (0.2)	0.6 (0.2)	0.83 (0.1)
	30	2.2 (0.1)	38.1 (0.9)	1.6 (0.5)	0.59 (0.06)	1.37 (0.72)
GRL10	5	9.8 (0.2)	4.3 (0.1)	25.7 (3.1)	0.33 (0.05)	0.38 (0.06)
	10	9.1 (0.9)	9.3 (4.6)	20.2 (4.9)	0.5 (0.2)	0.45 (0.2)
	15	7.1 (0.3)	14.2 (0.7)	13.1 (0.4)	0.75 (0.06)	0.54 (0.04)
	20	3.1 (0.1)	39.9 (8.3)	2.8 (0.7)	0.9 (0.1)	1.11 (0.41)
	30	–	–	–	–	–
GRL15	5	8.2 (0.6)	3.3 (1.4)	28.6 (3.8)	0.13 (0.03)	0.29 (0.06)
	10	8.1 (0.7)	9.0 (3.3)	23.8 (2.4)	0.4 (0.1)	0.34 (0.07)
	15	6.7 (1.0)	12.5 (7.8)	18.3 (4.3)	0.5 (0.3)	0.37 (0.18)
	20	5.5 (1.3)	12.9 (12.3)	14.3 (4.6)	0.2 (0.1)	0.38 (0.32)
	30	2.2 (0.7)	43.0 (4.6)	2.4 (1.4)	0.7 (0.2)	0.92 (1.88)

The percentages refer to the weight of starch and latex. All films contain 20% of glycerol w/w starch mass.

polyDMAEMA (which is alkaline) and readjusts the pH to 7.

The addition of modified natural rubber with 5% DMAEMA did not result in any visible difference in the mechanical properties the formed film, compared to those for the same amount of unmodified NRL, if the pH was such that the polyDMAEMA chains were uncharged (GRL5(n)). However, when the pH of the latex was decreased to 7 (by addition of hydrochloric acid before being added to the starch/glycerol solution), the tensile properties of the films were significantly changed. With a GRL5 content of 15%, the tensile strength and the elastic modulus dropped to 6.3 and 8.5 MPa, respectively, and the strain at break reached 16.2%, while with addition of 30% of GRL5(n) the strain at break was only 12.2% (Table 2). This trend continued when the GRL5 content was increased, with an increase in the elongation up to 38.1% and a large decrease in both tensile strength and elastic modulus.

At pH 7, there will be a significant number of positively charged units on the polyDMAEMA chains, as the pK_a of the monomer is ~ 9.4 [31]. These charged groups, many of which are on chains covalently linked to the polyisoprene [16], should increase the interactions between starch and rubber and would be expected to lead to a significant change in the mechanical properties of the composite material.

Indeed as shown in Table 2, the resulting films have a higher elasticity, high toughness (even for a small amount of latex), and high resistance to crack. Although the modified latexes contain significant amounts of ungrafted polyDMAEMA chains, the preceding argument suggests that the observed effects are dominated by grafted chains. It is highly unlikely that ungrafted chains could have a sufficient plasticizing effect to explain this significant change in material properties. The amount of polyDMAEMA compared to starch is low: e.g. a film containing 20% of GRL10 contains only 2% of polyDMAEMA. Literature data [32] show that much higher fractions are needed to affect significant property change in a blend (i.e. in the absence of grafting).

The observed effect of the amount of polyDMAEMA in the parent NRL shows that 10% gives good compatibility between the two phases. The addition of 20% of GRL10 gives high strain at break and the highest toughness (Table 2). With 30% of GRL10, the specimens were too rubbery to be tested: they exceeded the maximum elongation acceptable by the apparatus. NRL and GRL5(n) give relatively small decreases in the elastic modulus, while GRL5 and GRL10 lead to the greatest decrease, with GRL15 being intermediate (Table 2). This could be due to a larger amount of ungrafted water-phase polyDMAEMA in GRL15.

3.2. Dynamic-mechanical properties

The dynamic mechanical properties of a polymer blend give information on the degree of phase mixing. If the blends are immiscible, the $\tan \delta$ curves will show the presence of two damping peaks corresponding to the T_g s of the of the individual polymers [33]. If there is complete miscibility between the two polymer phases, only a single peak will be seen, lying between the T_g s of the component polymers. Broadening and shifts of the damping peaks are characteristic of partially miscible systems [34]. In the present system, any blending between the two main phases, starch and polyisoprene, will only be that induced by the relatively small amount of polyDMAEMA, which clearly could not lead to the sort of intimate blending seen in some other modified NRL systems where there is extensive grafting between both main phases [35]. It is important to recall that the maximum in $\tan \delta$ in DMA at some particular frequency (the value of T_d is of course frequency-dependent), which gives the dynamic transition temperature T_d , is less than the value of T_g as measured by DSC. This is because each technique measures different properties. DSC measures the change in heat capacity going from the ‘frozen’ to the ‘unfrozen’ chain, whereas DMA measures the change in mechanical response of these chains [36,37]; the two techniques give the effectively different averages of the complex dynamics of chain motion.

In the present system, there will be two T_g s and hence two T_d values in the parent polymers: those for (modified) natural rubber and the glycerol-plasticized starch. Fig. 1 shows the observed temperature dependence of $\tan \delta$ at 1 Hz between -100 and 0 °C for the reference starch/glycerol and a range of GRL blends with different amounts of polyDMAEMA, while Fig. 2 shows the corresponding loss moduli. The T_d for the reference film is ca. -48 °C, and similar values are obtained with the addition of NRL and of GRL5(n). The peak corresponding to the T_g of *cis*-

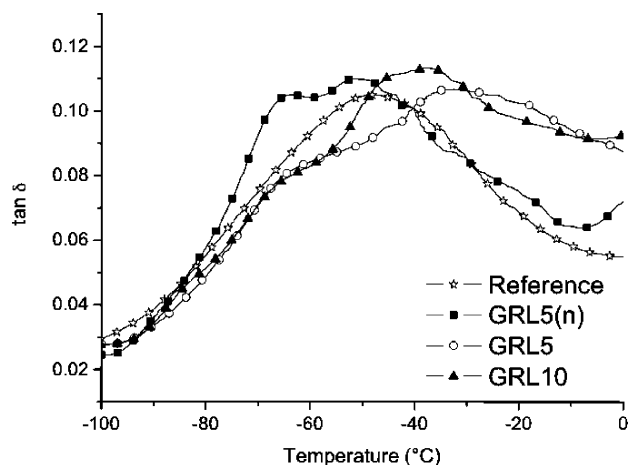


Fig. 1. Temperature dependence of damping ($\tan \delta$) for films containing 20% of the different latexes. The reference film comprises only starch and glycerol.

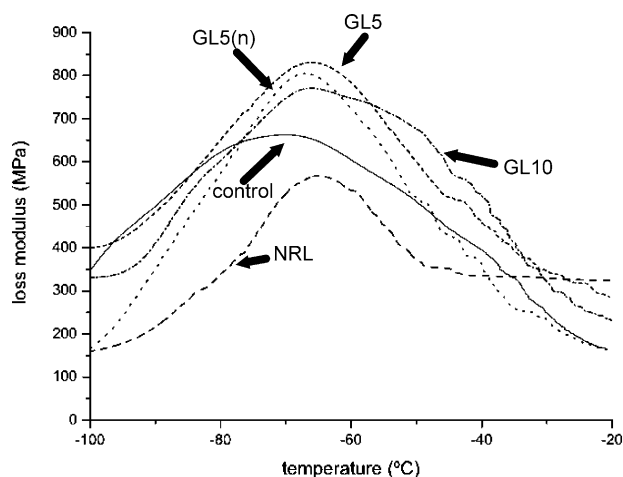


Fig. 2. Temperature dependence of loss moduli for films containing 20% of the different latexes. The reference film comprises only starch and glycerol.

polyisoprene is seen at -63 °C, and there is no significant change in the T_d for the starch, indicating insignificant interaction between the phases. When the pH of the GRL is such that the hydrophilic polyDMAEMA chains are charged, the thermo-mechanical behavior of the formed film is very different. The starch T_d increases to -38 and -32 °C with the addition of 20% of GRL5 and GRL10, respectively. This can be ascribed to strong interactions between the starch and the polyDMAEMA chains, whose T_g is ~ 10 °C [38]. This interaction extends to the rubber phase, as the NR peak becomes a small shoulder and the starch peak is somewhat broadened.

3.3. Film morphology

The freeze fracture of thick specimens of films containing 30% of NRL and GRL10 gives information on their internal structure, although it must always be borne in mind that any freeze-fracture micrograph is easily over-interpreted. For unmodified NRL, the latex particles are clearly visible in the starch matrix. The adhesion between the two phases is imperfect: some cracks appear on some of the particles edges (panel A of Fig. 3). With the grafted latex GRL10, containing 10% of polyDMAEMA, the internal structure of the film is clearly different. The particles are completely embedded in the matrix (panel B of Fig. 3). This is consistent with good compatibility between the fillers and the matrix induced by the presence of grafted cationic hairs.

The particles in panel C are larger than those in panel B, which is because of an adventitious selection on the TEM grids: NRL has a very broad range of particle sizes (from ~ 0.1 to 2 μm). It is also noted that adventitious selection of a grid area can lead to the erroneous impression that the GRL 10 blend micrographs indicate a higher amount of latex than for NRL. In fact the overall amounts are the same in all three samples. It is well known (e.g. [39]) that quantitative information from such micrographs requires examination of $\sim 10^3$ particles.

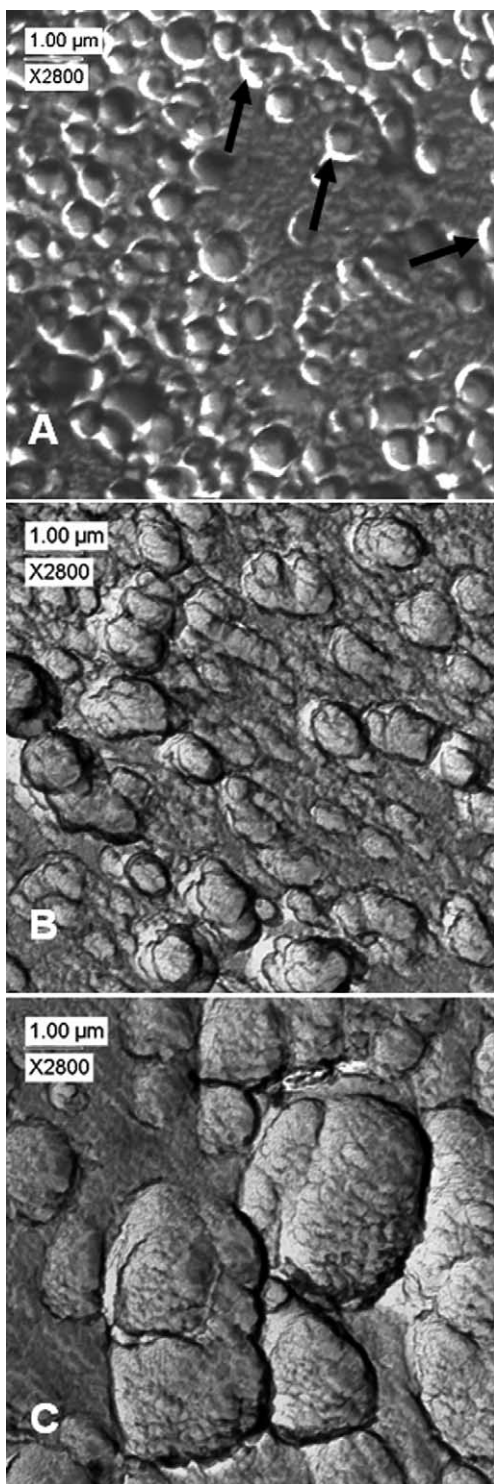


Fig. 3. TEM micrographs of freeze-fractured surfaces of films containing NRL (A) and GRL10 (B and C). Latex content is 30%. The arrows on panel A show some of the cracks on particles edges.

3.4. Hydrophobicity

The addition of hydrophobic particles to a hydrophilic component should enhance the water resistance of the resulting film, but this may be countered by the presence of

the hydrophilic polyDMAEMA. Results for contact angle are shown in Fig. 4, and for water adsorption in Fig. 5. The contact angles are greater than are typical for starch-based materials, which is not unsurprising given that a hydrophobic component is being added. With pure NRL the change is obvious. With up to 15% NRL, the contact angle with water increases for both the film face in contact with the air during the casting and for the other face, in contact with the polystyrene petri dish. With an addition of 20% of NRL, the angle tends to decrease, which possibly could be due some coagulation resulting in a weaker dispersion of the fillers in the matrix.

The addition of NRL renders the resulting film more hydrophobic, and also results in a net decrease of the water absorption of the material in a high-humidity atmosphere. After 24 h at 97% r.h. the mass gain of a film containing 20% of NRL is only 67% compared to the 88% of the reference film.

The chemical modification of NRL by DMAEMA causes the opposite effect even if the ratio of hydrophilic chains in GRL10 is only 10%. The contact angle decreases on both faces, and the water absorption greatly increases. This is because the cationic polyDMAEMA chains are even more hydrophilic than the starch and the interactions between them are not sufficiently strong to enhance the water resistance of the film.

Explanations for the dip in the curve of the water contact angle of the surface facing the polystyrene of the film containing 5% of GRL10 (which is reproduced with three separate samples) and water contact angle difference between the two faces of films containing modified latex have not yet been elucidated.

4. Conclusions

Films formed from the addition of two types of rubber latexes (natural rubber latex, and natural rubber latex grafted with ‘hairs’ of a cationic hydrophilic polymer, polyDMAEMA, the latter latex also containing ungrafted polyDMAEMA) to a glycerol/starch solution show a range of physical properties which can be explained by the competing effects of the hydrophilicity of the starch and the polyDMAEMA, the hydrophobicity of the NRL, and hydrogen bonding between the grafted polyDMAEMA and the starch. NRL acts essentially as inert filler: the tensile strength and modulus decrease and the elongation slightly increases. The adhesion between the phases is imperfect, and there is an increase in the hydrophobicity of the starch film.

The DMAEMA-modified NRL significantly changes the properties of the starch/latex films. In the cationic form, the polyDMAEMA chains enhance greatly the compatibility between the rubber and starch phases, with an optimum compatibility obtained for about 10% (w/w) DMAEMA relative to rubber. This leads to a large increase in film

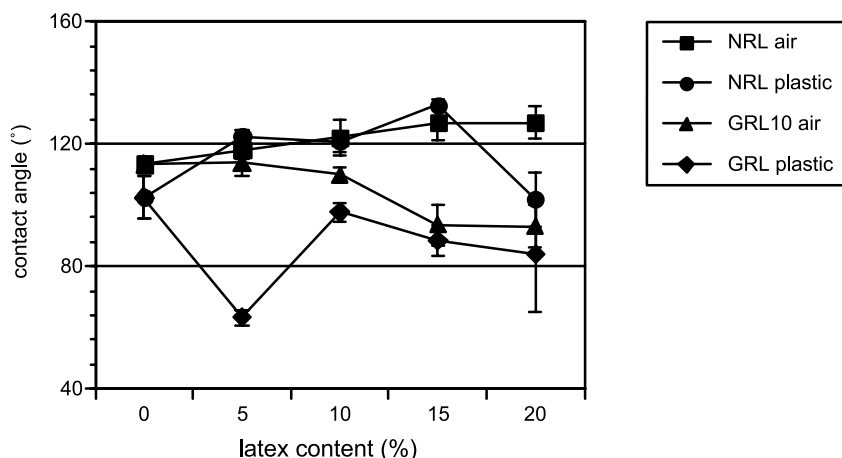


Fig. 4. Average contact angle and standard deviations for water on both surfaces of films, as a function of latex content.

elongation and toughness, but also in an increase of the water sensitivity of the composite material.

These results have potential applications in improvement of material properties of materials made from judicious addition of modified and unmodified NRL to polysaccharide-based agricultural 'waste' material.

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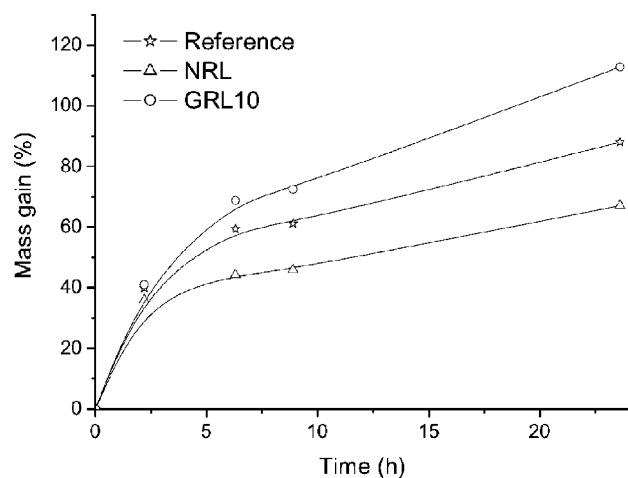


Fig. 5. Water absorption at 97% r.h. of films without latex, with 20% of NRL and with 20% of GRL10.

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