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Water vapour transmission in butadiene–MMA–methacrylic acid latex films

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Abstract

Batch emulsion copolymerizations of butadiene, methyl methacrylate (MMA), methacrylic acid (MAA) and hydroxy-ethyl methacrylate were performed in RC1e reactor, and the product vulcanized to form a film typical of those used for barrier products (gloves and condoms). The water vapour transmission (WVT) or breathability and physical properties (such as tensile strength and elongation at break) of the films were measured. Factorial design was used to vary the concentration of monomers in the copolymerizations. Methacrylic acid is a hydrophilic monomer and its distribution in or on the particles would be expected to affect WVT. Characterization by ultracentrifugation, nuclear magnetic resonance and infrared spectroscopy showed that most of the methacrylic acid units were buried inside the particles. This appears to be responsible for a relatively low WVT rate, probably due to the absence of hydrophilic (MAA-rich) domains inside the film. When centrifuged, the latex shows two particle-containing layers; characterization of the latex revealed the presence of MMA-rich domains in one layer, probably arising from secondary particle formation late in the polymerization. The buta-diene-to-MMA ratio probably dominates tensile strength through vulcanization with sulfur. The elongation at break was independent of both the butadiene-to-MMA ratio and the MAA concentration over the range studied (ascribed to competing effects), but dependent upon the total crosslinker concentration.
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1. Introduction

Barrier protection products (industrial gloves, surgical gloves and condoms) are made from synthetic and natural rubber latexes. The latex is then coagulated onto a mould ('dipping') and the

resulting film vulcanized (lightly crosslinked) to form the final barrier product. Natural rubber latex gives softness, adequate tensile strength, breathability and good elastic recovery, but a significant number of users develop allergic responses to the proteins found in natural rubber latex [1–5]. Although methods for reduction of the allergen content of natural rubber latex have been developed [6–12], they are expensive to implement and/or diminish desirable properties. Another disadvantage of natural rubber latex is the inability to 'fine-tune' the raw polymer in a way that effectively permits the engineering of infinite variations of the properties of synthetic latexes, a problem that has been only partly solved (e.g. [13–17]). Because of this problem, synthetic latexes are often used (e.g. [18]), but even then allergenicity is not entirely absent, for reasons just becoming clear [19]). These latexes contain relatively high amounts of a conjugated diene monomer (e.g. butadiene, which is comparable to natural rubber in terms of elasticity), a carboxylic-acid-containing monomer (e.g. methacrylic acid, MAA) and other monomers.

Vulcanization is an essential part of the process of manufacturing a barrier product, by generating a crosslinked network in the polymer matrix. There are two types of curing agents used for vulcanization. A traditional sulfur-curing agent can be used to covalently crosslink with the butadiene units in the polymer. Alternatively, the carboxyl groups can be ionically crosslinked via zinc ions, resulting in a high tensile strength in the formed films; the zinc oxide also acts as an activator for sulfur cross-linking reactions [20]. Furthermore, the carboxylic monomer enhances curing and wettability characteristics during the dipping process [21]. While many polymeric materials, such as natural rubber latex, poly(vinyl chloride), neoprene and "nitrile" (a carboxylated butadiene/acrylonitrile copolymer) have been successfully used in making gloves, all current materials suffer from one or more disadvantages, such as poor breathability or poor polar solvent resistance. There is no single material that can be used for all purposes.

The particular property of interest in the present paper is breathability or water vapour transmission (WVT), which is a measure of the rate at which water vapour passes through a polymer film. This property is important for comfortable usage. Despite its importance, breathability has been the subject of only a few publications in the open literature [22–28]. The chemical structure and film thick-ness of the polymer are the main determinants of the permeability of a film [27]. Five informative studies reveal some general principles, which guide the present work.

(1) Hayashi and co-workers [22] reported studies of multi-block polyurethane composed of poly(ethylene glycol) and hard segments of poly(4,4′-diphenylmethane diisocyanate) and poly(ethylene glycol)/poly(oxytetra methylene glycol). These polymers have high WVT rate (WVTR) above the glass transition temperature (T_g) and low WVTR below T_g. The WVTR was dependent on the ethylene glycol concentration, the ethylene glycol being the softer and more hydrophilic segment.

(2) Sun and Lee [23] reported sorption/desorption properties of water vapour on the hydrophilic poly(2-hydroxyethyl methacrylate), poly (HEMA). The sorption of water was postulated to involve hydrogen bond formation between a water molecule and two hydroxyl groups in the polymer. However, the data suggested that the process was a complex one even for this homopolymer, depending on the state of water, the polymer relaxation behaviour (related to T_g), and the interactions between water and polymer.

(3) Schuman et al. [24] investigated the influence of characteristics such as the degree of crosslinking, T_g and degree of carboxylation in carboxylated styrene–butadiene latexes on the tensile properties and WVTR. There was a slight tendency for WVTR to decrease with increasing crosslinking. The degree of carboxylation had no pronounced influence on the barrier properties, but there was a slight tendency for WVTR to decrease with increasing amounts of carboxylic groups. One expects that increasing the amount of hydrophilic units, as carboxylic groups, would increase the WVTR. The slight decrease of WVTR in this work suggests that a low WVTR was because of a rather high gel content. There may then be an optimum degree of carboxylation to ensure that the material is hydrophilic enough but not overly crosslinked.

(4) Yang et al. [26] synthesized a block copolymer of hydroxyl-terminated polybutadiene and a polyurethane, which exhibited a higher WVTR than the pure polyurethane. They postulated a permeation of water through the

samples in two steps: water vapour adsorbing on the surface and then diffusing through the membrane. They explained the higher WVTR in the copolymer by a more extensive adsorption of water vapour on the surface of the copolymer than on pure polyurethane.

(5) Stroeks et al. [27,28] studied water permeability of segmented block poly(ether-*b*-ester) based breathable films by using two methods: ASTM E96B and ASTM E96BW. In the ASTM E96BW test, the film is in direct contact with water while in the ASTM E96B test an air layer exists between film and water. Water permeability was found to depend on film thickness, polymer type, relative humidity and also of the presence or not of stagnant air layers surrounding the film.

In the present study, the WVTR and mechanical properties of latexes of butadiene/methyl methacrylate/methacrylic acid copolymers is investigated. Butadiene is hydrophobic, methyl methacrylate (MMA) is slightly hydrophilic, and MAA is hydrophilic. The recipe is based on a patent [29] and has similarities with the latexes of Schuman et al. [24]. Since Schuman et al. observed that WVTR does not increase linearly with the degree of carboxylation, the effects of butadiene-to-MMA ratio and of MAA concentration over WVTR and mechanical properties are systematically investigated here using a factorial design [30]. The thrust of this work is to relate the end-use properties of butadiene-based latexes to the molecular architecture of the polymer backbone.

The distribution of the MAA inside or on the surface of latex particles gives different properties to the final end-use products. This distribution [31–34] depends upon the reactivity ratios among the monomers, their concentration, the pH and feed regime used in latex synthesis. The amount of MAA in the water phase will depend on the same factors. If MAA units are located on the surface of the particles, this would be expected to enhance the colloidal stability of the latex and thus to increase the critical coagulation concentration during dipping. On the other hand, if most of the methacrylic acid units are buried inside the particles, the physical crosslinking between Zn ions and MAA units after film formation may be reduced. The spatial distribution of the MAA units in the films probably strongly influences the WVT and hence breathability.

2. Experimental

2.1. Materials

Butadiene (Bd), potassium persulfate, *tert*-dodecyl mercaptan, tetrapotassium pyrophosphate, naphthalene sulfonic acid, ethylenediaminetetraacetic acid and sodium dodecylbenzene sulfonate (reagent grade, Aldrich) were used without further purification. Methyl methacrylate (MMA), methacrylic acid (MAA) and hydroxyethyl methacrylate (HEMA) (reagent grade, Aldrich) were purified by passing through a basic alumina column to remove inhibitor. Water was demineralized with QPAK 1 columns from Milli-Q. 2-Butanone (MEK) was used as a gel content measurement solvent. Nitrile glove (TNT) and polyurethane wound dressing film were used as standard films for WVTR.

Compounding chemical ingredients such as a clear coagulant formulation (containing primarily 40% calcium nitrate) and a 50% latex compounding curative paste containing conventional sulfur accelerators, were used as supplied by Ansell.

2.2. Syntheses

Batch emulsion polymerizations of butadiene, MMA and MAA (with or without HEMA) were performed in a Mettler RC1e reactor under pressure. Potassium persulfate and sodium dodecylbenzene sulfonate (SDBS) were used as initiator and surfactant, respectively. *tert*-Dodecylmercaptan was used as a chain transfer agent. All chemicals except butadiene and potassium persulfate were bubbled through with high-purity argon in the reactor to eliminate inherent oxygen. After depressurization, butadiene (a gaseous monomer at room temperature) was transferred to the RC1e reactor

Table 1
Standard polymerization recipe

Ingredient	Monomer concentration, phm
Demineralized water	150
Dodecylbenzene sulfonic acid	2.75
Ethylenediaminetetraacetic acid	0.05
Naphthalene sulfonic acid	0.1
Tetrapotassium pyrophosphate	0.1
tert-Dodecylmercaptane	0.6
Potassium persulfate	0.25
Butadiene	70
Methyl methacrylate	25
Methacrylic acid	5

phm = part per hundred monomer.

with the vessel temperature at 25 °C and stirrer speed at 300 rpm. The temperature was then raised to 52 °C for the reaction. After heater calibration for 1 h 45 min, the initiator solution was pumped into the reactor. The reaction was allowed to run to complete conversion, monitored using the heat flow profile on the RC1e (see Supplementary material). The standard recipes used throughout this study are based on Suddaby's patent [29], varied using factorial design (see below). A standard recipe used for the syntheses is shown in Table 1.

2.3. Latex compounding and dipping

Quantities are indicated in parts per hundred dry rubber, phr. Solid content, pH and viscosity of the original latex were measured, and the pH of the latex was adjusted to 8.5 by addition of a 5 wt% potassium hydroxide aqueous solution. Next, 30 wt% SDBS solution (0.72 phr) was added to the latex (100 phr) followed by the addition of the compounding paste (total 3.5 phr accelerator) under slow stirring. The mixture was left for 24 h under gentle stirring, permitting air bubbles to rise to the surface while preventing creaming and skin formation. Before dipping, the total solid content of latex was adjusted to 35–37% using demineralized water. Solid content, pH, particle size and viscosity of the latex were measured after mixing.

A plate dipping former (mould) (8 cm width, 18 cm length and 0.5 cm depth) was cleaned by sequential dipping into diluted weak base, weak acid and hot water, then dried at 70 °C for at least half an hour. The former was then dipped into a heated coagulant solution at 55 °C. After the temperature of the former dropped to around 40 °C, it was dipped into the compounding latex. After air drying for a few minutes, the former coated with the latex was placed in warm water to remove residual latex and serum, then placed in an oven at 70 °C for 15 min to allow pre-curing, and finally transferred to another oven at 120 °C for 30 min to allow complete curing.

3. Analysis techniques

3.1. Experimental design

Factorial design [30] was used to draw conclusions from the experiments and to establish how the input parameters affected the final results. This technique is based on statistical assumptions concerning replication and randomization to minimize experimental

Table 2
Design matrix and monomer concentration

Run no.	Factor A Bd/MMA ratio	Factor B [MAA]	Run label	Monomer concentration, phm			
				Bd	MMA	MAA	HEMA
1	1.375	2	(1)	72.21	25.79	2	–
2	2.8	2	a	56.74	41.26	2	–
3	1.92	3.5	0	63.49	33.01	3.5	–
4	2.8	5	b	70	25	5	–
5	1.375	5	ab	55	40	5	–
6	–	–	–	57	39	2	2
A	TNT nitrile glove, a copolymer of Bd, acrylonitrile and MAA, provided by Ansell S&T, Malaysia						
B	Wound dressing film, polyurethane, provided by Ansell S&T, Malaysia						

variability from run to run. The aim of the present study is to investigate the effect of monomer composition on WVTR and tensile properties (tensile strength and % elongation at break). The simplest factorial design of type 2^k is used in the present study: the 2^2 factorial design; with two factors A and B, each at two levels. The factors were butadiene-to-MMA ratio (A), and MAA concentration (B). The total amount of monomers was kept the same for all recipes; thus, total monomer concentration is not an independent factor. The design matrix is shown in Table 2. The low and high levels of factor A (dimensionless) were 1.375 (70/25) and 2.8 (55/40), respectively. The low level of factor B was 2 phm (parts per hundred monomer) and the high level was 5 phm. The centrepoint was 1.92 (62.5/32.5) of factor A and 3.5 phm of factor B. The low and high levels of each factor were selected from the 'preferable' range given in Suddaby's patent [29].

The viscosity of the polymer latexes was measured using a Brookfield DV-II+ viscometer. A Malvern HPPS 3.3 light-scattering particle sizer was used to measure the z-average particle size of latex samples.

3.2. Solid content

The solid content of the latexes was measured by gravimetry. A few drops of latex were put in an aluminium pan and dried for 24 h in an oven at 60 °C.

3.3. Gel content

The gel content is the insoluble fraction of rubber that is crosslinked; however, a reported value of gel content always depends on the details of the

technique chosen to measure this quantity. The gel content of the latexes was determined following ASTM D3616-82. Firstly, the latex was cast in a Petri dish and left to dry at room temperature for 5 days to achieve a constant weight of the film. A small piece of about 0.15 g was cut from the dry film and then immersed in 15 mL of butan-2-one (also named methyl ethyl ketone, MEK) for 24 h. Exactly 5 mL of liquid was then pipetted into an aluminium pan and dried to constant weight. The gel content was calculated as the ratio of the dried weight after and before leaching with MEK.

3.4. Tensile testing: tensile strength and percentage elongation at break

The specimen was prepared by cutting a film in a rectangular shape of 5 mm × 8 cm. The length between bench markers (the two marks placed on the specimen and used to measure elongation or strain) was approximately 5 cm. The exact dimensions of the specimen (width, length and thickness) were measured again before carrying out the testing. The specimen was placed in an Instron model 5567 Universal Testing device, using a stretching rate of 500 mm min^{-1} until the specimen ruptured. The film sample thickness was ~1.8–2.5 mm and tensile strength and percent elongation at break measured.

3.5. Glass transition temperature

The glass transition temperature (T_g) of the copolymer films were measured by using a DSC 2920 MDSC v. 2.6 A. The sample was heated to 80 °C, then cooled to −80 °C, then heated from −80 °C to 80 °C at 5.0 °C min^{-1} under liquid nitrogen. The predicted T_g of copolymers was calculated from the Fox equation (e.g. [35]) and also using Pochan et al.'s relation [36].

3.6. Permeability: water vapour transmission (WVT)

WVTR was measured based on the ASTM E96-66 procedure, as follows. The environment inside a glove bag was maintained at 50 ± 2% relative humidity throughout the duration of the experiment by using a saturated aqueous solution of $Ca(NO_3)_2$, which gives 51% humidity at 24.5 °C. The experiment was performed at 23.5–24.5 °C. A small fan was put inside the glove bag to generate air circulation as recommended in the ASTM procedure and an air velocity of around 0.15–0.25 m s^{-1} above

the Payne cup (measured with an anemometer); the air velocity specified in the ASTM procedure is between 0.02 and 0.3 m s^{-1}. The thickness of a film sample was measured by a micrometer for at least 5 points, near the centre of the film specimen and at the centre of each quadrant. Film thicknesses were around 1.8–2.5 mm. The dried sample from the oven was put in the glove bag for at least 2 h before the experiment was conducted in order to equilibrate the sample with the atmosphere moisture inside the glove bag. Sample weight increased initially with time when taken from the oven and placed inside the glove bag (see Supplementary material). Demineralized water was put into a permeability Payne cup (2.5 cm diameter). The water level was kept 2 cm from the specimen to avoid contact between the specimen and the water. The film then was attached on the Payne cup. The cup with the film was placed on a balance, which was located in the glove bag. The weight change as a function of time was measured every 5 min for at least 2 h. The WVTR rate was calculated as:

$$\text{WVTR} = \frac{G}{t \cdot A} \tag{1}$$

where G is the weight change, t is the time and A is the test area.

3.7. Determination of acid distribution in particles

Latex samples were centrifuged after addition of sucrose at 9×10^4 rpm at 5 °C for 4 h in a Beckman Coulter Optima L-100 Ultracentrifuge. Three phases were then obtained after ultracentrifugation: a sedimentary latex (located on top of the centrifuge tube), a white liquid (located in the middle) and the aqueous phase (located at the bottom).

The amount of acid in the discrete phase was measured using Fourier-transform infrared spectroscopy (FTIR). The white liquid obtained from centrifugation was freeze-dried under vacuum for 24 h. A dry residual solid was analyzed by FTIR in bulk. Near-IR spectra were taken with a Bruker IFS66v FTIR spectrometer in absorption mode in the region 500–4000 cm^{-1}.

The sedimentary latex did not redisperse completely in water or dissolve in common solvents.

3.8. Nuclear magnetic resonance

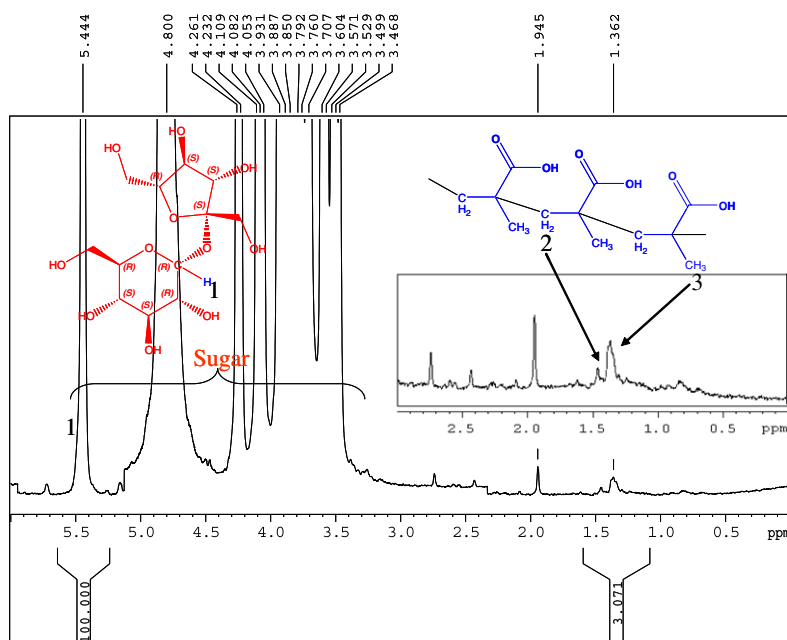The aqueous phase from ultracentrifugation was freeze-dried under vacuum for 24 h. A dry residual

Fig. 1. ^{1}H NMR spectrum of the aqueous phase of Run 5 in D$_2$O.

solid was then dissolved in deuterium oxide at 10 mg mL^{-1} for 24 h before quantifying the acid using NMR. Quantitative ^{1}H NMR spectra were recorded at room temperature on a Bruker Avance spectrometer operating at a ^{1}H Larmor frequency of 300 MHz, with a 5 mm QNP (^{1}H–^{19}F/^{31}P/^{13}C) probe. 100 transients were recorded with a 6.2–6.4 μs 90° pulse and a 25 s relaxation delay. It was checked that this relaxation delay was long enough for proper relaxation by comparing one of the spectra with a spectrum recorded with a five times longer relaxation delay; identical spectra were obtained. The spectra were internally referenced through residual HOD signal at 4.80 ppm. A reference spectrum of sucrose in D$_2$O was also recorded under the same conditions. Its αH signal comes out at 5.4 ppm. The

chemical shifts assignment for relevant signals of poly(MAA) and sucrose are detailed on Fig. 1. The quantity of acid was calculated by integration and comparison of the signals between 1.1 and 1.6 for the poly(MAA) (5H), and between 5.25 and 5.55 ppm for the sucrose (1H).

4. Results and discussion

4.1. Effect of monomer composition on physical properties

Monomer concentrations variations were chosen to follow a 2^2 factorial design [30] as a polynomial approximation model, which assumes smooth and continuous output and independent factors. The

Table 3
Properties of the various polymer films: tensile strength, elongation at break, WVTR (with the standard deviations SD) and glass transition temperature

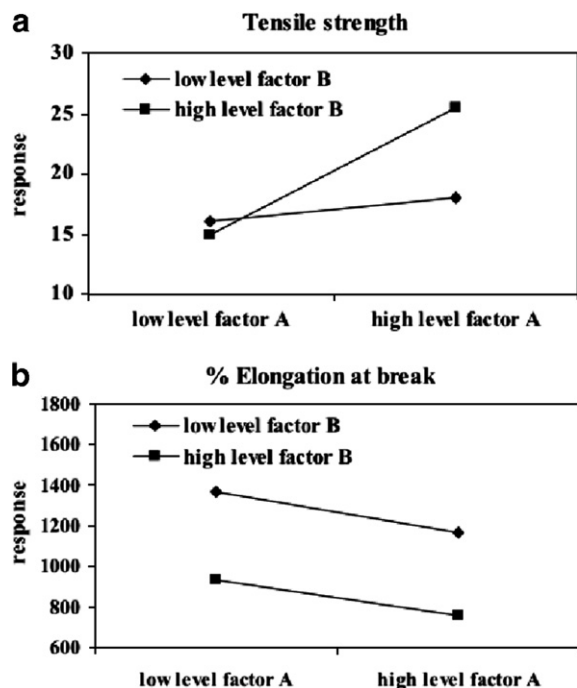| Run no.	Tensile strength (MPa)		Elongation at break (%)		WVT (g/24 h/m^2)		T_g (°C)	
	Value	SD	Value	SD	Value	SD	Experimental	Predicted
1	16	1.1	1370	28.3	21	5.44	−55	−52
2	18	1.2	1170	33.1	23	3.43	−38	−31
3	30	2.4	1010	65.3	20	4.30	−43	−40
4	15	2.2	974	72.6	21	4.80	−51	−49
5	25.5	4.2	772	24.2	16	7.09	−28	−27
6	–	–	–	–	19	–	−39	−31
A	–	–	–	–	44	–	–18	–
B	–	–	–	–	792	–	–	–

a

b

Fig. 2. Dependence of response data from Table 4 against factor A for both levels of factor B, (a) tensile strength, (b) % elongation at break.

basic concept is to create homogeneous blocks in which the 'nuisance' factors are held constant and the factors of interest are allowed to vary. A primary purpose of the factorial design experiments is to select or screen out the few important main effects from the many less important ones. In this study, we investigated the effect of monomer composition on tensile strength, elongation at break,

and WVTR. Ranges of monomer concentrations were selected based on the preferable concentration ranges listed in Suddaby's patent [29]: see Table 2 (Runs 1–5).

After vulcanization, an elastomeric poly(butadiene-*co*-MMA-*co*-MAA) copolymer film is obtained. Vulcanization introduces dimensional stability, reduced creep and flow, and permits the manufacture of a wide range of rubber articles. The higher is the degree of crosslinking, the higher is the tensile strength and the lower is the extensibility. Polybutadiene has a low T_g (−83 °C) [37], while poly(MMA) and poly(MAA) have high T_g values (105 °C and 162 °C, respectively) [37]. Table 3 shows the results of tensile strength and elongation at break for various monomer compositions.

A single replicate of the experimental design was run. A design matrix and the response data obtained from a single replicate of the 2^2 experimental design are shown, respectively, in Tables 2 and 3. Due to only one replicate being performed, there was no internal estimate of error. Using an error mean square is inappropriate in this case. A simple method suggested by Montgomery [30] to examine a normal probability plot of the estimates of the effects can be difficult to interpret for small data sets. Trend plots and interactions plots gave the clearest understanding of the causal relationships between input and output variables in this design.

Factorial design results for tensile properties are shown in Table 3 and illustrated graphically in Figs. 2 and 3. The results in Fig. 2a show that the difference in response for tensile strength between the levels of one factor is not the same at all levels of the
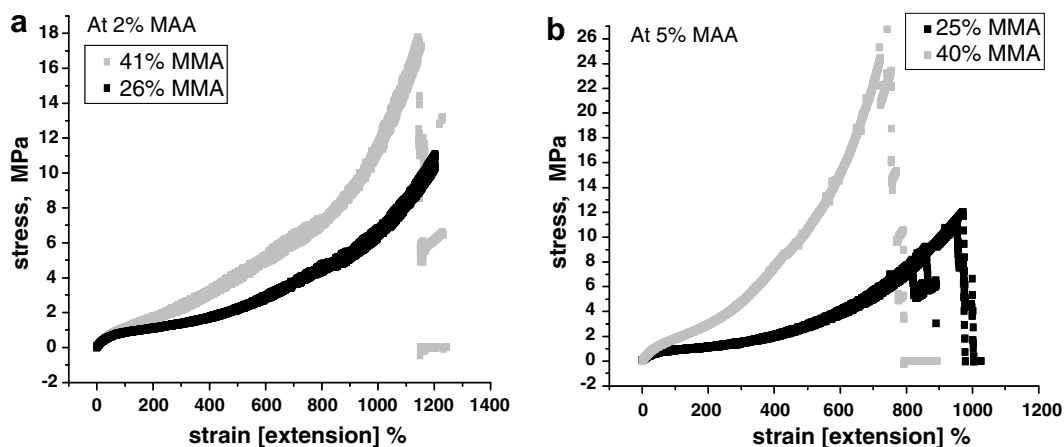

Fig. 3. Stress against strain at different MAA concentrations, (a) 2%, (b) 5%.

other factors. An interaction between these two factors is inferred because the lines at low and high levels are not parallel.

Tensile properties are probably the most frequently considered, evaluated and used throughout the industry. These properties indicate polymer behaviour under loading tension. Tensile strength is the maximum force when tension stress is applied to polymer in order to elongate it to the point where it ruptures. Crosslinks introduced by vulcanization are chemical crosslinks of pendant double bonds from diene units by sulfur and ionic crosslinks of zinc ions to acid functional group. Additionally, there are other physical crosslinks in the form of polymer gel, e.g. arising from entanglements. This type of crosslink generally increases the tensile strength of the copolymer film. The ionic crosslinking that occurs during vulcanization is related to ratio of MAA to Zn^{2+}. During vulcanization, zinc oxide can act as an activator for sulfur crosslinks and in addition decompose into Zn^{2+}, which gives an ionic crosslink. Thus, zinc oxide concentration should have a stronger influence on the tensile strength than sulfur concentration. Vulcanized films showing higher elongation at break generally exhibit lower tensile strength. Elongation at break also depends upon the stretching rate (lower elongation at faster rate). Further independent experiments confirmed that tensile strength increased with increasing ZnO amount (see Supplementary material).

The assumption of using two-level factorial designs is linearity in the factor effects. A 'centrepoint' run (Run 3, with label "0") was added to check the possible curvature and stability of the process. A reasonable hypothesis is that tensile strength should increase as a function of MAA and butadiene concentrations. There was however no noticeable trend in the data, and inclusion of the centrepoint gives non-monotonic behaviour: a maximum. This non-monotonic behaviour can arise for a number of reasons [21]. The total concentration of all crosslinks influences the mechanical properties of the vulcanizates, but changing concentrations of the various species also changes both gel content (see Table 4) and molecular weight and branching distributions. Consistent measurements of molecular weight and branching distributions are hard to obtain consistently in systems of this type [34,38] because crosslinked polymer does not dissolve in any solvent and was not attempted here. In analyzing the data on latex properties in Table 4, account

Table 4
Latex properties

| Polymer | Properties | | | | |
	Solid content (%)	Gel content (%)	Viscosity (cP)	pH	Particle size (nm)
1	41	62	87.9	4.65	97
2	38	37	24.3	4.87	95
3	41	30	51.2	4.61	103
4	40	47	24.5	4.42	96
5	37	49	26.9	4.60	82

had to be taken of the observation that the gel content of any batch was not consistent. Furthermore, the magnitude of the tensile strength maximum, and the crosslink concentration at which it occurs, are expected to depend upon the chemical nature of the covalent crosslink introduced during vulcanization. As is well known, the restriction of mobility by crosslinking interferes with film formation. Elongation at break is influenced by the total crosslinking in the vulcanized polymer. Fig. 4c and d show the response data of % elongation at break against factors A and B. The results showed the opposite trend to tensile strength, as expected. The two factors seem to be independent of each other.

By looking only at low or high levels of MAA concentration (Fig. 3), further inferences could be made as follows. Tensile strength increased with increasing MAA concentration while % elongation at break showed the opposite trend, which corresponds to the ionic crosslink arising between MAA and Zn ions.

4.2. Effect of monomer composition on WVTR

Breathability or moisture permeability of film is measured by the amount of moisture that can pass through the film in 24 h under appropriate conditions. Numerical results are detailed in Table 3. Fig. 5 shows the interaction between factor A and factor B. High moisture permeability requires the film to exhibit high water absorption and/or a high water vapour diffusion coefficient. Both functions require a continuous amorphous phase in which T_g is well below room temperature (or application temperature). In this case the lack of a dominant effect can be explained as a compromise between rubbery behaviour in the amorphous phase (low T_g due to the butadiene content), and mechanical properties (related to MAA content, which gives ionic crosslinking). This is consistent with inferences
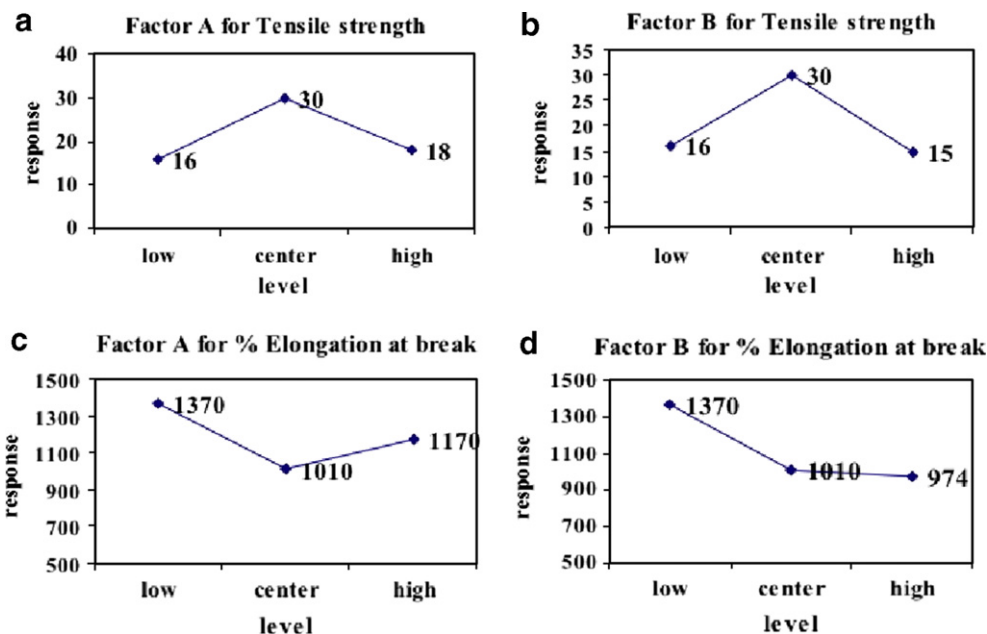
Fig. 4. Dependence of response on main effect for both levels and centrepoint, (a) factor A for tensile strength, (b) factor B for tensile strength, (c) factor A for elongation at break, (d) factor B for elongation at break.
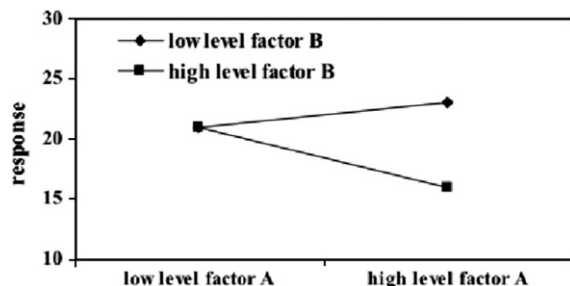

Fig. 5. Dependence of WVT response data in Table 3 on factor A for both levels of factor B.

from a number of studies [27,28,39] which report high WVTR in thermoplastic elastomers composed of alternating polyether and polyester segments, in which variations were made in the hard/soft ratio, the block length of the polyether and the type of polyether. The amount and the type of soft block strongly affect the breathability, and the amount and type of hard block affect the mechanical properties. The WVTR of this type of material (wound dressing film) was measured (Table 3) and is a decade higher than that of glove materials.

Before conducting these experiments, it was hypothesized that increasing the amount and type of hydrophilic monomer should increase the trans-portation of water vapour through the film. However, within the experimental range examined here, the WVTR was not significantly increased (Fig. 6). Therefore the investigation of where the hydrophilic monomer units are located in the particle and how this affects the WVTR were seen to be important in understanding the present system.

HEMA was judged to be an appropriate hydrophilic monomer to test the preceding hypothesis. Incorporation of this monomer into the butadiene–MMA–MAA copolymer was expected to enhance WVTR. Results reported in Table 3 show that this was not the case, and indeed copolymers containing HEMA seemed to have a lower WVTR than those without. The WVTR of commonly used nitrile films, made from carboxylated butadiene acrylonitrile copolymers, is higher than that of the present butadiene–MMA–MAA copolymers (see Table 3). The higher hydrophilicity of polyacrylonitrile compared to poly(MMA) might be one reason for the higher WVTR of nitrile film. However, the difference might also arise from different microstructures.

4.3. Investigation of location of MAA by conductimetry and ultracentrifugation

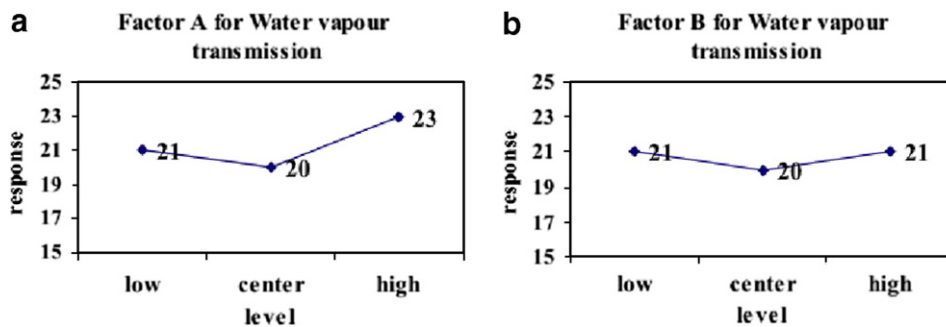Understanding of the latex morphology, and especially the location of the hydrophilic monomer

Fig. 6. Dependence of WVT response on main effect for both levels and centrepoint, (a) factor A, (b) factor B.

MAA in the particles and in the film, would provide information about the mechanisms of WVTR. To this end, the distribution of MAA groups is usually investigated by conductometric titration of the latex [33,34,40]. This is indeed the only technique which allows a direct quantification of the acid groups located at the surface of the particles. Since there were many types of acids in the system (dodecylbenzene sulfonic acid, ethylenediaminetetraacetic acid and naphthalene sulfonic acid as well as MAA), these acids all influence the conductivity of the system, resulting in no clear inferences being possibly drawn from conductance as a function of added base (see Supplementary material). In the case of complex/industrial formulations, it is thus not possible to determine directly the concentration of acids at the surface of the particle by conductimetry. Advanced characterization techniques such as capillary electrophoresis may offer possibilities in the future. Indirect characterization after separation by ultracentrifugation has been carried out in this work. It was found that the density of the discrete (copolymer) phase of the untreated latex was very close to that of the continuous phase, so that a good separation between phases by centrifugation could only be achieved if the density of the continuous phase was changed. A 35 wt% of sucrose solution was added in order to increase the aqueous phase density to 1.15 g mL^{-1}. Three phases were then obtained after ultracentrifugation: a sedimentary latex, a white liquid and the aqueous phase (located at the bottom).

4.4. Investigation of the aqueous phase by NMR

NMR was used in order to determine the MAA concentration in the aqueous phase. The ^{1}H NMR spectrum of aqueous phase of Run 5 in D$_2$O at room temperature is shown in Fig. 1. All the latexes give spectra comparable to this one. Characteristic signals of sucrose appeared between 3 and 5.5 ppm, the ones of poly(MAA) at 1.36 and 1.45 ppm corresponding, respectively, to CH$_3$ and CH$_2$. Those signals have been reported at 1.0 and 1.1 ppm in D$_2$O at room temperature by Sugai et al. [41]. However, as PMAA is ionizable, the pH of its solution in D$_2$O has a strong influence on the measured chemical shifts [42]. The discrepancy between the values measured in the present work and by Sugai et al. are postulated to arise from a difference in pH [42] or from the interaction of the hydroxyl functional group in sucrose and the carboxyl groups in poly(MAA) (in this case there was an excess of sucrose compared to the poly-(MAA) concentration) or from a difference in tacticity of the polymers (as already observed for PMMA [43]).

Integration to determine the concentration of poly(MAA) was based on the addition of a known amount of a reference compound. In this study, the signal at 5.4 ppm was chosen as the standard signal, corresponding to sucrose –CH, as shown in Fig. 1. The characteristic signals of poly(MAA) at 1.36 and 1.45 ppm were used to determine the concentration of poly(MAA) and poly(HEMA). The characteristic peaks of poly(HEMA) that correspond to the backbone CH$_3$ and CH$_2$ are similar to those of poly(MAA) [43]. The concentration of poly(MAA) and poly(HEMA) left in the aqueous phase of any single batch was very small compared to the initial concentration (see Table 5). This means that MAA must be located either on the surface of or inside the sedimentary latex particles, or in the white phase. For the copolymer of butadiene–MMA–MAA–HEMA, the aqueous-phase polymer concentration includes both MAA and HEMA units but remains negligible compared to their initial concentrations.

Table 5
The concentration of poly(MAA) and poly(HEMA) in aqueous phase of various latexes

| Run	Initial [MAA], mmol L^{-1}	NMR experiments	
		[MAA] in AQ phase, mmol L^{-1}	[MAA] in AQ phase, wt% of the initial concentration
1	0.198	1.6×10^{-3}	0.8
2	0.230	2.4×10^{-3}	1.0
3	0.162	2.7×10^{-3}	1.6
4	0.092	3.1×10^{-3}	3.4
5	0.091	4.7×10^{-3}	5.1
6	0.142	2.6×10^{-3}	1.8

Concentration is in per litre of continuous phase in latex.

4.5. Investigation of the white phase by infrared spectroscopy

The white liquid phase obtained from ultracentrifugation could possibly comprise a homopolymer or copolymer containing hydrophilic monomer as a major component. Such a hydrophilic copolymer might not be compatible with polybutadiene at the start of polymerization, and thus might not be incorporated into the particles.

FTIR spectra are shown in Fig. 7. The FTIR spectrum of sucrose at 20 °C shows the broad band of hydroxyl groups at 3500–3000 cm^{-1} and other sharp bands in the fingerprint region at 1500–500 cm^{-1}. Those peaks were found in the FTIR spectra of every white liquid sample. The characteristic peaks of polybutadiene [44,45] normally appear around 1640–1680 cm^{-1} for the C=C stretch (the *cis*-isomer is at 1660 cm^{-1}, the *trans*-isomer is at 1675 cm^{-1}, and the C=C stretch of the pendant group is at 1640 cm^{-1}). These peaks were barely apparent in any sample from the white liquid phase; the level of butadiene monomer unit is thus below the detection limit. However, there was a short region between 1800 and 1500 cm^{-1} that allowed the other components to be identified (Fig. 8).
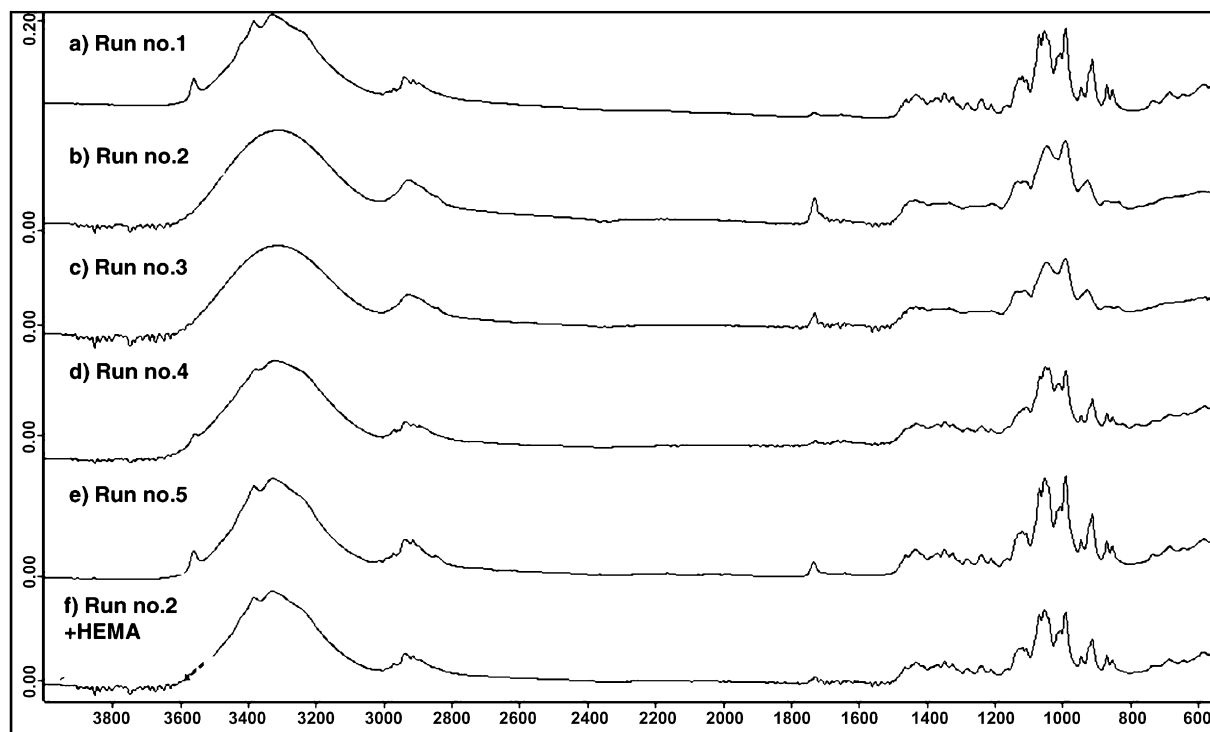
Fig. 7. FTIR spectrum of white liquid phase of all latexes (abcissa is wavenumber/cm^{-1}).

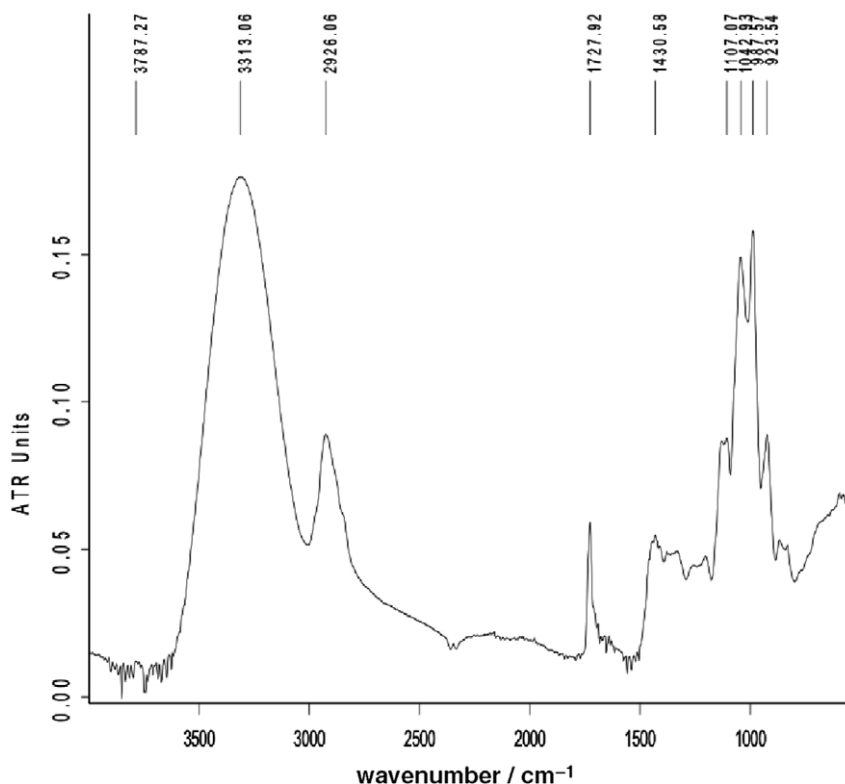Fig. 8. FTIR spectrum of white liquid phase from Run 2.

The dominant characteristic peak of poly(MMA) [46,47] is generally a C=O stretch at 1730 cm⁻¹. Every spectrum of the white liquid phase showed this type of peak, proving that there was some in this phase. In general, FTIR can distinguish the different functionalities better than other methods. For poly (MAA), the C=O stretching of the carboxyl group [48] normally appears at around 1700 cm⁻¹ but this peak was not observed here. There were no significant different signals between the films of the copolymers of butadiene–MMA–MAA–HEMA and the one of butadiene–MMA–MAA. The white liquid thus contains sucrose plus a significant fraction of poly(MMA). Further evidence that supports this conclusion is the ultracentrifugation itself. The density of the sedimentary latex was around 1.03 g cm⁻³ (depending on the monomer composition) [37] and could thus not be precipitated by ultracentrifugation in pure water. The density of the aqueous phase after adding sucrose was 1.15 g cm⁻³. Most of the latex particles precipitated, except this white phase. The white phase should thus have a density close to 1.15 g cm⁻³. The density of homopoly(MMA) [37] is ∼1.16 g cm⁻³ and is

thus consistent with the white phase being mainly composed of poly(MMA). The measured glass transition temperatures are also consistent with this conclusion (see Section 4.6).

After separation by ultracentrifugation, no significant amount of MAA can be detected either in the aqueous phase or in the white phase. The MAA groups are thus located in the sedimentary latex. If a significant amount of MAA groups was located on the surface of the particles, they could form hydrophilic domains in the polymer films (the Zn²⁺ should contribute to the formation of these domains during the compounding process [49]). Water may then go through the film by moving from one hydrophilic domain to the other. In the mechanism postulated by Wang et al. [50], hydrophilic domains at the surface of the film are necessary for a high WVTR because the water needs to adsorb on the surface of the film before diffusing through it. It might be expected that the hydrophilic monomer (MAA) would be primarily located on the particle surface. However, the distribution of acid groups in latexes is influenced by several factors that depend on polymerization conditions [32,34]. At

low pH, MAA is in the unionized, and therefore less hydrophilic, form. Moreover, under certain conditions, high molecular weight poly(MAA) can undergo a coil-to-globule or coil-to-rod transition [51], and in a compact form, it would be unlikely to provide adequate electrosteric stabilization. In the present work, the polymerization was carried out from an initial pH of ca 3.5 to a final pH of ca 4.6. The pKa of MAA is 4.66 at 20 °C [37], thus most of the MAA monomer is unionized and therefore is likely to be mostly buried inside the particles [34]. This is the most likely explanation for the low WVTR measured on these latexes.

4.6. MMA-rich domains

The separation by ultracentrifugation of two types of particles, including some MMA-rich ones is surprising. However, it is confirmed by the DSC measurements. The glass transition temperatures of the copolymer films are reported in Table 3. Predicted glass transition temperatures were calculated based on two different equations: Fox's equation (based on free-volume changes) and Pochan's equation [34,36]. Pochan's equation predicts values noticeably different from the experimental ones (see Supporting Information). The present results fitted well with the predictions of Fox's equation (see Table 3). For polymers 2 and 6, the experimental T_g values were however much lower than the theoretical values, which could mean that there was less MMA incorporated into the copolymer than calculated from the original ratio of the different monomers; this is consistent with the finding that there was a separate MMA-rich phase, discussed below. The applicability of the Fox equation can be inter alia ascribed to the light crosslinking in the samples from the present study having no major effect on short-range chain mobility.

The amount of MMA-rich phase is visually significantly lower than the sedimentary phase. This amount can not be determined by gravimetry because of the presence of the sucrose. It is too low for the DSC to detect its T_g. However, it is possible to estimate the quantity of MMA in the sedimentary phase using the experimental value of the T_g corresponding to this phase and the Fox equation (weight fraction of MMA is then the unknown). The difference between the initial amount of MMA and the amount detected in the sedimentary phase gives an estimate of the amount of white phase. The white phase represents 1 and

5 wt% of the total solid content for runs 5 and 2, respectively, and 2 wt% for the other runs.

The presence of this MMA-rich phase can be partially explained by the kinetics of polymerization. The reactivity ratios r_1 and r_2 for butadiene and MMA, respectively are reported to be both lower than unity, but with r_1 greater than r_2 [37]. Initial amounts of butadiene and MMA are similar (especially in Run 2). Butadiene should be consumed faster than MMA. The MMA-rich phase (white liquid phase in ultracentrifugation) could then be formed at the end of the polymerization when a negligible amount of butadiene is left and MMA is then the major component. This poly (MMA) phase could well comprise MMA-rich particles formed by secondary nucleation, probably by homogeneous nucleation, which is not unexpected with a monomer such as MMA which has a high propagation rate coefficient [52] and moderate water solubility [53,54].

The presence of these MMA-rich domains was not expected. The hydrophilicity of MMA is probably too low for these domains to contribute significantly to water vapour transmission.

5. Conclusions

Factorial design experiments on factors affecting usage properties of interest for personal barrier products in poly(butadiene-*co*-methyl methacrylate-*co*-methacrylic acid) films, formed after crosslinking with ZnO and other vulcanization reagents, were used to examine how tensile strength of butadiene–MMA–MAA copolymer film is influenced by the MAA concentration. The zinc ions from zinc oxide were expected to ionically crosslink with the carboxyl groups of MAA during vulcanization to enhance the crosslinking and thus the tensile strength. However, it was demonstrated instead that the butadiene-to-MMA ratio probably dominates tensile strength through vulcanization with sulfur. On the other hand, the elongation at break of copolymer was independent of both the butadiene-to-MMA ratio and the MAA concentration but dependent upon the total crosslinking concentration.

An important property of personal barrier products is breathability, measured as water vapour transmission (WVT). The WVT of poly(butadiene-*co*-MMA-*co*-MAA) was governed by the ratios of the monomer in the system, balanced to have enough rubbery component (butadiene) as well as

good mechanical properties (related to the amount of MMA and MAA).

The relatively low WVTR in the films examined here is not due to any homopoly(MAA) formed during synthesis in the aqueous phase, which was found to be very small. Ultracentrifugation of the latex led to three distinct phases: a solid, a water phase and a white liquid phase. This last phase contained a large amount of poly(MMA), probably formed by secondary particle formation late in the polymerization. NMR and FTIR analysis suggested that most of the hydrophilic monomers (MAA and HEMA) were located in and/or on the particle, and are probably buried within the particle and do not form extensive hydrophilic domains, which otherwise would enhance WVT. The WVTR could thus be improved by locating the hydrophilic monomers at the interface, replacing MAA by a more hydrophilic monomer at low pH (e.g. acrylic acid) or surfmers. The MMA-rich particles proved also non-significant in term of WVTR. MMA could also be replaced by a more slightly more hydrophilic monomer such as HEMA or *N*-vinyl-pyrrolidone.

Acknowledgements

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.eurpolymj.2007.11.009.

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