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Synthesis of poly(vinylidene chloride)-based composite latexes by emulsion polymerization from epoxy functional seeds for improved thermal stability

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ABSTRACT

Poly(glycidyl methacrylate-*co*-butyl methacrylate)/poly(vinylidene chloride-*co*-methyl acrylate) (poly(GMA-*co*-BMA)/poly(VDC-*co*-MA)) composite latexes have been successfully synthesized via a two-stage emulsion polymerization process. In a first step, emulsion copolymerization of GMA and BMA was carried out in optimized conditions (low temperature, neutral pH, starved-feed conditions) to both limit the hydrolysis of epoxy groups and obtain small particle size (typically 30–50 nm size range). Composite latexes were then obtained by a second-stage seeded copolymerization of VDC and MA in the presence of tetrasodium pyrophosphate to control the pH and reach high molecular weight, leading to partial encapsulation of the seed particles (snow-man morphology, in agreement with theoretical expectations). Thermogravimetric analyses performed on the resulting composite particles showed that the epoxy-functionalized seed polymer behaved as an efficient thermal stabilizer of PVDC.

1. Introduction

Poly(vinylidene chloride) has been studied from both academic and industrial points of view, due to its outstanding properties, including a good resistance to a wide variety of solvents and an extremely low permeability to water, oxygen [1] and aroma [2] originating from its high degree of crystallinity [3,4]. This characteristic makes it a good candidate for use in the high barrier packaging industry. However, PVDC homopolymer undergoes a fast degradation when heated a few degrees over its melting temperature ($T = 203$ °C) [5], resulting in a gradual coloration and a loss of its superior properties. At moderate temperatures ($T = 120$–190 °C) slow degradation occurs which also deteriorates the beneficial properties, HCl being the only gas product evolved. The dehydrochlorination mechanism, described in Scheme 1 consists then in an unzipping process [6–9], starting from defect structures identified as unsaturation randomly introduced in the polymer backbone during polymerization or processing [7,8,10]. The homolytic cleavage of allylic C—Cl bonds gives rise to a chlorine radical that abstracts an adjacent hydrogen atom to release hydrogen chloride and extend the unsaturation by one unit, creating a new allylic C—Cl bond that will further propagate the degradation reaction in a similar way.

In order to enhance the thermal stability of the polymer, vinylidene chloride is usually copolymerized with small percentages of other monomers [6], typically acrylates, vinyl chloride or acrylonitrile. Nevertheless, this strategy is limited as increasing amounts of comonomers tend to decrease PVDC barrier properties. Therefore, to further limit the thermal degradation of poly(vinylidene chloride) copolymers, the addition of thermal stabilizers has to be considered. Improvement of thermal stability is particularly required for waterborne PVDC: emulsion polymerization leads to vinylidene chloride copolymers with a poor thermal stability compared to their counterparts obtained by suspension, solution or bulk polymerizations [3,4], due to the presence of larger amounts of additives accelerating the polymer degradation process.

We report here a strategy consisting in the incorporation of epoxy-functionalized seed particles into PVDC latexes via a two-stage emulsion polymerization process. Although their role in the stabilization of vinylidene chloride copolymers is not well understood, epoxy-functionalized compounds, such as epoxidised soybean oil or glycidyl methacrylate (co)polymers, have been

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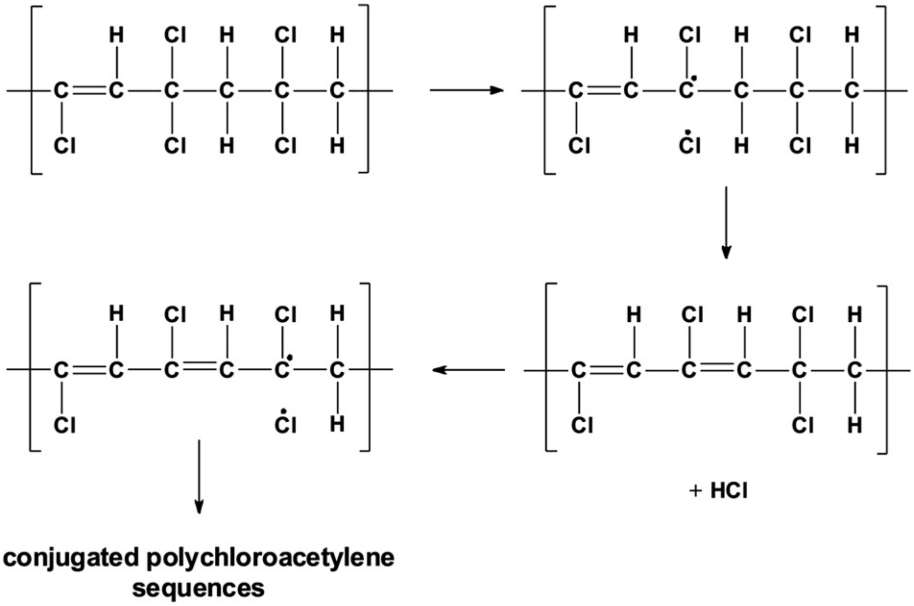

Scheme 1. Mechanism of poly(vinylidene chloride) dehydrochlorination.

proved to retard the polymer thermal degradation [3,4,11,12]: they may not only behave as efficient HCl-scavengers but also as chelating agents for metal chlorides, which are formed in situ via a reaction between hydrochloric acid and metal ion impurities and behave as catalysts for PVDC dehydrochlorination [13,14].

To the best of our knowledge, it is the first time that PVDC composite particles, showing improved thermal stability, have been prepared from epoxy-functionalized seed latexes.

2. Experimental

2.1. Materials

Glycidyl methacrylate (GMA, Aldrich, 97%), *n*-butyl methacrylate (BMA, Acros, 99%), vinylidene chloride (VDC, Aldrich, 99%) and methyl acrylate (MA, Aldrich, 99%) were distilled under reduced pressure to remove inhibitors. Potassium persulfate (KPS, Aldrich, 99%), sodium metabisulfite ($Na_2S_2O_5$, Aldrich, 99%), sodium hydrogencarbonate ($NaHCO_3$, Aldrich,), tetrasodium pyrophosphate (TSPP, Alfa Caesar, 98%), Dowfax 2A1 (Dow, 42 wt% solution in water) were used as received. Water was deionised through an ion-exchange resin (conductivity below 1 mS/cm).

2.2. Polymerizations

Emulsion copolymerization of glycidyl methacrylate and butyl methacrylate was carried out in a 250 mL double-walled glass vessel, equipped with a mechanical glass anchor propeller. An aqueous solution of sodium metabisulfite, Dowfax 2A1 and sodium hydrogencarbonate was charged in the reactor, heated up at 30 °C and stirred at a speed of 200 rpm. At the beginning of the reaction, 9 mL of a 10 g/L aqueous solution of KPS was injected at once in the reactor followed by a continuous addition of this solution at a rate of 4.5 mL/h for 4 h. At the same time a continuous feed of the monomer solution (90 wt% of GMA, 10 wt% of BMA) was started and maintained for 3 h. Continuous additions were performed with two Perfusor Compact syringe pumps (Braun). The reaction lasted for 5 h in total.

Seeded emulsion copolymerization of vinylidene chloride and methyl acrylate was performed in a 300 mL stainless steel reactor (Parr Instrument Company), equipped with a stainless steel 4-bladed mechanical stirrer and internal pressure and temperature sensors. Oxygen was removed from the autoclave by purging it via three cycles of vacuum (10^{-2} mbar) broken with nitrogen. Vacuum was restored in the reactor before charging an aqueous solution containing the poly(GMA-*co*-BMA) seed latex and sodium metabisulfite. A 4 bars nitrogen overpressure was then established in the vessel. The speed of agitation was set at 250 rpm and the temperature was raised to 55 °C. A stirred pre-emulsion containing tetrasodium pyrophosphate, KPS, Dowfax 2A1, VDC and MA, was then continuously pumped into the reactor at a rate of 24 mL/h for 5 h via a Series III digital HPLC pump (LabAlliance). The overall reaction lasted for 6 h. Residual monomer was stripped by heating up the latex for 1 h at 60 °C under reduced pressure (0.2–0.4 bar). The protocol for the synthesis of the reference latex (R1) consisted in adding an initial shot of 15 wt% of the pre-emulsion and 10 mL of a 10 g/L KPS aqueous solution to form a poly(VDC-*co*-MA) seed in situ. After 30 min, the pre-emulsion continuous addition was started and maintained at a rate of 24 mL/h for 5 h.

2.3. Characterization

2.3.1. Particle size measurements

The particle sizes distributions of the latexes were determined by dynamic light scattering (DLS) with a Nanotrac particle size analyzer (Microtrac Inc.).

2.3.2. Gel content

The percentage of gel present in the poly(BMA-*co*-GMA) copolymers was determined by extraction of the soluble part with dichloromethane. A sample of dry polymer (w_{polymer}) was weighted in a cellulose extraction thimble (Whatman) of known mass, placed in a Soxhlet and extracted with dichloromethane at reflux for 72 h. At the end of the extraction, the undissolved part of the polymer remaining in the thimble was dried and weighted ($w_{\text{undissolved part}}$). The gel content was then calculated via Equation (1):

$$\textit{gel content}(\%) = W_{\text{undissolved part}} \times 100 / W_{\text{polymer}} \tag{1}$$

Table 1
Polymerization recipes to study the influence of temperature and pH on the hydrolysis of epoxy groups.

			Initial load				KPS solution feed (4.5 mL/h)		Monomer feed (10.3 g/h)
Entry	T (°C)	pH	$Na_2S_2O_5$ (g)	$NaHCO_3$ Buffer (g)	Dowfax 2A1 (g)	Water (g)	KPS (g)	Water (g)	GMA/BMA (g)/(g)
S1	60	6.3	0	0	8.04	73.70	0.27	27	27.82/3.08
S2	30	3.4	0.25	0	8.01	73.52	0.27	27	27.85/3.06
S3	30	7.3	0.24	0.09	8.00	72.83	0.27	27	27.71/3.10

2.3.3. *Titration of epoxy groups*

The determination of the polymer epoxy content is based on the ring-opening of epoxy groups by HBr, generated in situ by a reaction between tetraethylammonium bromide and perchloric acid. A known mass of dry polymer (typically 0.1 g for the seed polymer and 1 g for PVDC composite samples) was placed in a beaker and dissolved in 60 mL of dioxane for 5 min at 80 °C, before adding 60 mL of acetic acid. Once the beaker was back to room temperature, 10 mL of a 0.1 N solution of tetraethylammonium bromide in acetic acid was added. The titration by a 0.1 N perchloric acid solution in acetic acid was followed by pH-metering. By comparing the experimental and theoretical epoxy contents, the percentage of epoxy groups preserved from hydrolysis during the polymerization could be determined.

2.3.4. *Determination of molecular weights of P(VDC-co-MA) copolymers*

Molecular weights of the second-stage poly(VDC-*co*-MA) copolymer were determined by Gel Permeation Chromatography (PL-GPC 50, Varian, Inc.). Freeze-dried samples of composite and reference latexes were dissolved in THF and filtered on 0.2 mm PTFE filters, before being injected in the SEC apparatus. A calibration employing polystyrene standards ($K = 14.1 \times 10^{-5}$ dL/g and $\alpha = 0.7$) [15] was employed to calculate the molecular weights. Mark-Houwink coefficients determined by Revillon et al. [16] for poly(VDC-*co*-MA) copolymers with a 80:20 VDC:MA mass ratio ($K = 35 \times 10^{-5}$ dL/g and $\alpha = 0.57$) were employed to exploit the calibration curve.

2.3.5. *TEM microscopy*

Composite latexes were diluted as following: 2 droplets in 100 mL of DI water. The sample was deposited on a copper grid covered by a layer of FORMAR (polyvinyl formal), then dried at room temperature and under air atmosphere. Pictures were obtained using a Zeiss EM910 (80 kV) microscope.

2.3.6. *Thermal degradation*

The thermal degradation of PVDC powders (obtained by freeze-drying of the composite latexes) was analyzed on a TGA apparatus Q50 (TA Instruments). Analyses consisted of isothermal experiments performed for 120 min at 160 °C under air atmosphere.

3. Results and discussion

3.1. *Synthesis of epoxy-functionalized seed latexes*

Hydrolysis of epoxy groups is a major point to consider when performing the emulsion (co)polymerization of glycidyl methacrylate for two main reasons [17]: on the one hand, it obviously decreases the polymer epoxy-functionality and on the other hand, hydrolysis of glycidyl methacrylate to glyceryl methacrylate, a water-soluble monomer, may affect the emulsion polymerization process and results in the formation of water-soluble polymer. It is known that the ring-opening reaction of epoxy groups in water occurs through both acidic and basic catalyses, and is promoted by high temperatures. A preliminary study, employing recipes indicated in Table 1, was undertaken in order to determine conditions of temperature and pH that enable to limit the hydrolysis of epoxy groups.

HBr titrations carried out on freeze-dried samples of latexes confirmed the sensitivity of epoxy groups to temperature and pH (Table 2): a high temperature (60 °C) and a pH close to neutral point resulted in the loss of about 10% of the polymer epoxy content, while an acidic pH at low temperature (30 °C) provoked the hydrolysis of epoxy groups to a similar extent.

The low pH (pH = 3.4) obtained when performing the polymerization reaction at 30 °C in presence of sodium metabisulfite originates from the formation of two equivalents of bisulfite radicals ($\cdot SO_3H$, pKa ≈ 1.9) per dissociation event [18] (Equation (2)), while the thermal dissociation of potassium persulfate only leads to the formation of low amounts of bisulfate ions (HSO_4^-, pKa = 2.0) originating from the transfer of $SO_4^- \cdot$ radicals to water [18] (Equation (3)).

$$S_2O_5^- + S_2O_8^{2-} + H_2O \rightarrow 2SO_4^{2-} + 2\cdot SO_3H \tag{2}$$

$$S_2O_8^{2-} + xH_2O \rightarrow (2-x)SO_4^- \cdot + xHSO_4^- + xHO\cdot \tag{3}$$

where x depends on the extent of transfer of $SO_4^- \cdot$ radicals to water ($0 < x < 2$)

Hence sodium hydrogencarbonate $NaHCO_3$ was employed as a buffer to compensate for the acidity brought about by bisulfite radicals and maintain a pH close to 7 throughout the polymerization reaction. The HBr titration indicated that more than 98% of epoxy groups were preserved from hydrolysis in these conditions of low temperature and neutral pH.

The gel content determined by continuous extraction of the polymer soluble part in dichloromethane was close to 99% in all cases, independent of temperature or pH conditions. Geurts et al. [17] established that the high gel content observed in methacrylic latexes containing GMA originated from traces of dimethacrylates present in glycidyl methacrylate. Considering that they obtained very low sol contents (from 2 to 8%) when performing the emulsion copolymerization of GMA and BMA in a 10:90 GMA:BMA mass ratio, it is not surprising to observe an even lower sol content when working with a 90:10 GMA:BMA mass ratio in our case.

Epoxy-functionalized seed latexes with controlled particle size were obtained by starved-feed emulsion copolymerizations of glycidyl methacrylate and butyl methacrylate, following the recipes given in Table 3.

Table 2
Influence of the reaction temperature and pH on the hydrolysis of epoxy groups.

Entry	T(°C)	pH	Polymer gel content (%)	Measured epoxy content[a]	Theoretical epoxy content[a]	Intact epoxy groups (%)
S1	60	6.3	99.0	0.571	0.633	90.2
S2	30	3.4	98.5	0.557	0.634	87.9
S3	30	7.3	99.2	0.622	0.633	98.3

[a] The epoxy content is expressed in number of mol of epoxy groups per 100 g of polymer.

Table 3
Polymerization recipes for the synthesis of epoxy-functionalized latexes at 30 °C.

Entry	Initial load				KPS solution feed (4.5 mL/h)		Monomer feed	
	$Na_2S_2O_5$ (g)	$NaHCO_3$ (g)	Dowfax 2A1 (g)	Water (g)	KPS (g)	Water (g)	GMA/BMA (g)/(g)	Feed rate (g/h)
S4	0.25	0.10	8.03	73.25	0.27	27	27.06/3.04	batch
S5	0.25	0.09	8.04	73.47	0.27	27	44.86/4.72	16.8
S6	0.25	0.10	8.04	73.23	0.27	27	36.03/4.03	13.4
S7	0.26	0.11	8.01	73.29	0.27	27	30.50/3.40	11.3
S3	0.24	0.09	8.00	72.83	0.27	27	27.71/3.10	10.3
S8	0.25	0.10	8.02	73.52	0.27	27	19.40/2.23	7.2

A batch reaction was first carried out to follow the monomer conversion versus time (Fig. 1). Following experiments employed monomer feed rates ($R_{feed} < 16.8$ g/h, *i.e.* $R_{feed} < 4.3 \times 10^{-4}$ mol L^{-1} s^{-1}) much lower than the maximum rate of polymerization observed during the batch experiment ($R_{p\ max} = 1.5 \times 10^{-3}$ mol L^{-1} s^{-1}). Instantaneous monomer conversions higher than 90% obtained along the reaction S5 confirmed that monomer-starved conditions were fulfilled for feed rates lower than 16.8 g/h.

The seed latex particle size could then be adjusted by varying the monomer feed rate. According to the Smith-Ewart theory [19], the number of particles formed during the nucleation phase is given by Equation (4):

$$N_P = k \times (\rho/\mu)^{0.4} \times (a_s S)^{0.6} \tag{4}$$

Where ρ is the rate of radical generation, μ the rate of particle volume growth, a_s the area occupied by one surfactant molecule and S the amount of surfactant present in the medium in the form of micelles. As a result, reducing the monomer feed rate parameter should decrease the particle volume growth rate and lead to a higher number of particles nucleated, resulting in a lower average particle diameter. Although our system does not strictly obey the model proposed by Smith and Ewart, this tendency is confirmed by values of D_P (intensity-averaged particle diameter) presented in Table 4.

3.2. Synthesis of PVDC composite latexes in presence of epoxy-functionalized seeds

Poly(GMA-*co*-BMA) latexes were then employed as seeds for the second-stage emulsion copolymerizations of vinylidene chloride and methyl acrylate. Table 5 indicates the amounts of reactants employed for these reactions.

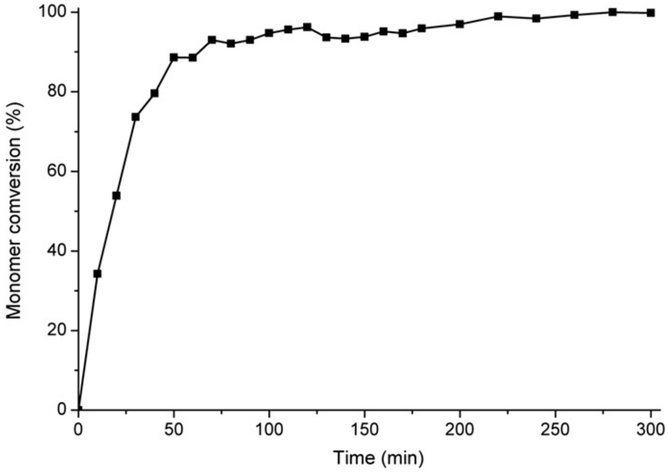

Fig. 1. Monomer conversion curve for the batch emulsion copolymerization of GMA and BMA at 30 °C (Entry S4 in Table 3: $Na_2S_2O_5 = 0.25$ g, $NaHCO_3 = 0.10$ g, Dowfax 2A1 = 8.03 g, Water = 100.25 g, KPS = 0.27 g, GMA = 27.06 g, BMA = 3.04 g).

The stability of epoxy groups was still a serious factor to consider when performing the emulsion copolymerization of vinylidene chloride and methyl acrylate since the evolution of hydrochloric acid from PVDC chains to the water phase already started during the polymerization reaction. Tetrasodium pyrophosphate (TSPP) was thus employed to scavenge HCl molecules and protect epoxy groups from ring-opening reactions. As indicated in Table 6, when TSPP was not included in the recipe, the polymerization reactions occurred in acidic conditions (pH of about 2) and at least 80% of epoxy groups were hydrolyzed, while the addition of TSPP enabled to maintain a pH close to 5 all along the reaction and preserve more than 80% of epoxy groups.

At first sight, the differences between molecular weights (Table 6) of poly(VDC-*co*-MA) polymers synthesized in the presence or absence of TSPP may be striking, considering that similar monomer/initiator ratios were employed in all recipes. However, the pH values measured on final latexes may account for this divergence, given that the dissociation of potassium persulfate is strongly catalyzed by protons in acidic conditions [20–22]. Indeed, the rate of dissociation of KPS can be expressed by Equation (5) that takes into account the process of acid-catalysis:

$$k_0 = k_1 + k_2[H^+] \tag{5}$$

k_0 dramatically increases at low pH, leading to a higher rate of radical generation which explains the lower polymer molecular weights obtained in absence of TSPP.

The composite latex morphology was another significant feature to consider, as it may affect the properties of the final material. The graphical representation developed by Gonzalez-Ortiz et al. [23] provided a thermodynamic prediction of the composite particles structure, by taking into account the surface tensions γ_{ij} at the interfaces of the three phases present in the system (first-stage polymer (1), second-stage polymer (2) and water (w)). The surface tension values of water [24], PGMA [25] and PVDC [24] (as approximation of poly(VDC-*co*-MA) copolymer) and their corresponding polar and dispersion components γ_i^P and γ_i^D (Table 7) were used to derive the values of γ_{ij} (by applying the harmonic-mean Equation (6) established by Wu [24]), T and U (Table 8). According

Table 4
Influence of the monomer feed rate on the number of nucleated particles.

Entry	Monomer feed rate (g/h)	Final wt% of polymer	Particle diameter D_P (nm)	Total number of particles N_P ($\times 10^{17}$)
S5	16.8	31.49	86.0	1.38
S6	13.4	26.89	70.2	2.05
S7	11.3	23.73	50.6	4.63
S3	10.3	22.13	42.9	6.90
S8	7.2	16.54	28.0	17.42

Table 5
Recipes for the seeded emulsion copolymerization of vinylidene chloride and methyl acrylate at 55 °C.

Entry	Employed seed latex	Initial load			Pre-emulsion feed (≈32 g/h)					
		$Na_2S_2O_5$ (g)	Seed latex (g)	Water (g)	TSPP (g)	KPS (g)	Dowfax 2A1 (g)	VDC (g)	MA (g)	Water (g)
C1	S9[a]	0.20	4.18	27.97	0.39	0.33	3.31	84.07	9.32	62.75
C2	S9[a]	0.18	4.19	28.00	0	0.33	3.31	84.31	9.31	62.91
C3	S3[b]	0.23	6.60	32.22	0.35	0.39	3.33	82.15	9.00	65.35
C4	S10[c]	0.19	8.48	29.82	0	0.34	3.38	84.91	9.82	57.87
C5	S7[d]	0.20	9.94	31.96	0.37	0.35	3.78	85.46	9.65	58.70
C6	S6[e]	0.21	10.34	32.09	0	0.34	3.33	86.06	9.43	57.53
R1 (ref)	None	0.20	0	18.27	0.06 +0.31	0.12 +0.35	0.50 +2.86	12.72 +72.09	1.42 +8.02	21.50 +53.81

[a] Seed polymer content: 22.0%, seed particle diameter: 43.0 nm, pH = 7.5.
[b] Seed polymer content: 22.1%, seed particle diameter: 42.9 nm, pH = 7.3.
[c] Seed polymer content: 22.0%, seed particle diameter: 50.0 nm, pH = 7.1.
[d] Seed polymer content: 23.7%, seed particle diameter: 50.6 nm, pH = 7.4.
[e] Seed polymer content: 26.9%, seed particle diameter: 70.2 nm, pH = 7.5.

Table 6
Characteristics of composite and reference PVDC latexes.

Entry	Seed content (%)	TSPP	Latex pH	Monomer conversion (%)	M_n (g/mol)	M_w (g/mol)	M_w/M_n	Epoxy content (mol/100 g)	Theoretical epoxy content (mol/100 g)	Intact epoxy groups (%)
C1	1.00	yes	6.2	95.9	61,500	176,400	2.87	4.5×10^{-3}	5.6×10^{-3}	80.4
C2	0.98	no	2.1	98.2	12,900	36,300	2.80	0	5.5×10^{-3}	0
C3	1.65	yes	5.4	94.6	60,300	155,600	2.58	9.0×10^{-3}	10.4×10^{-3}	86.5
C4	1.99	no	2.2	97.7	9900	25,000	2.52	0	11.2×10^{-3}	0
C5	2.54	yes	5.8	95.5	67,300	182,800	2.72	12.7×10^{-3}	14.3×10^{-3}	88.7
C6	2.87	no	2.5	99.2	10,600	25,300	2.39	2.6×10^{-3}	15.9×10^{-3}	16.5
R1	0	yes	3.7	92.5	50,100	135,400	2.70	/	/	/

Table 7
Surface tension values of water, PGMA, PBMA and PVDC and their corresponding polar and dispersion components.

	Surface tension γ ($N.m^{-1}$)	Polar component γ^P ($N.m^{-1}$)	Dispersion component γ^D ($N.m^{-1}$)
Water [24] (w)	72.8	50.7	22.1
PGMA [25] (1)	40.14	32.68	7.46
PBMA [26] (1′)	31.20	4.93	26.27
PVDC [24] (2)	45.40	9.08	36.32

to this diagram applied to our case (Fig. 2), a PGMA seed would only be partially engulfed by the second-stage poly(VDC-*co*-MA) polymer, resulting in a snowman-like morphology.

$$\gamma_{ij} = \gamma_i + \gamma_j - \left[4\gamma_i^P\gamma_j^P \Big/ \left(\gamma_i^P + \gamma_j^P\right)\right] - \left[4\gamma_i^D\gamma_j^D \Big/ \left(\gamma_i^D + \gamma_j^D\right)\right] \quad (6)$$

According to the same graphical representation applied to the case of a less polar first-stage polymer such as poly(n-butyl methacrylate) (PBMA) [26], the seed particles were expected to be fully encapsulated by the second-stage PVDC polymer, leading to a core–shell morphology. Therefore, we assumed that employing poly(GMA-*co*-BMA) as the first-stage copolymer would encourage the encapsulation process.

Transmission electron microscopy (TEM) enabled to visualize the structure of poly(GMA-*co*-BMA)/poly(VDC-*co*-MA) composite particles. Snowman morphologies observed on pictures (Fig. 3) showed that poly(GMA-*co*-BMA) seed particles were partially encapsulated by the second-stage poly(VDC-*co*-MA) copolymer: thus, the first-stage copolymerization of GMA with BMA was not sufficient to favour the encapsulation process.

Table 8
Values of γ_{ij}, U and T calculated from the harmonic-mean equation.

	γ_{12} ($N.m^{-1}$)	γ_{1w} ($N.m^{-1}$)	γ_{2w} ($N.m^{-1}$)	$U = \gamma_{12}/\gamma_{2w}$	$T = \lvert\gamma_{2w}-\gamma_{12}\rvert/\gamma_{1w}$
PGMA/PVDC	32.36	11.15	32.44	0.998	0.007
PBMA/PVDC	2.84	38.02	32.44	0.088	0.779

3.3. Thermal properties

Powders obtained by freeze-drying of reference and composite latexes were subjected to thermogravimetric analyses to compare their thermal stabilities (Fig. 4). After a temperature ramp of 20 °C/min during 8 min, the variation of the sample mass was measured at 160 °C for 120 min under air atmosphere. The composite particles clearly exhibited a slower degradation than the reference sample, indicating that the presence of epoxy-functionalized seeds

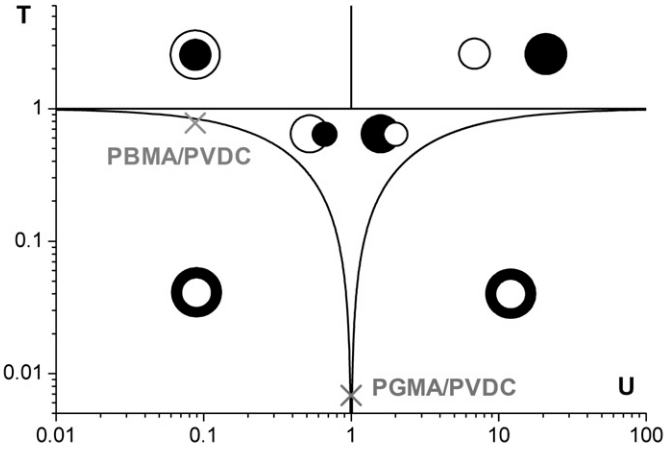

Fig. 2. Graphical representation for the prediction of the thermodynamic morphology of PGMA/PVDC and PBMA/PVDC composite particles ($U = \gamma_{12}/\gamma_{2w}$, $T = |\gamma_{2w} - \gamma_{12}|/\gamma_{1w}$). □: seed/first-stage polymer, ■: second-stage polymer.

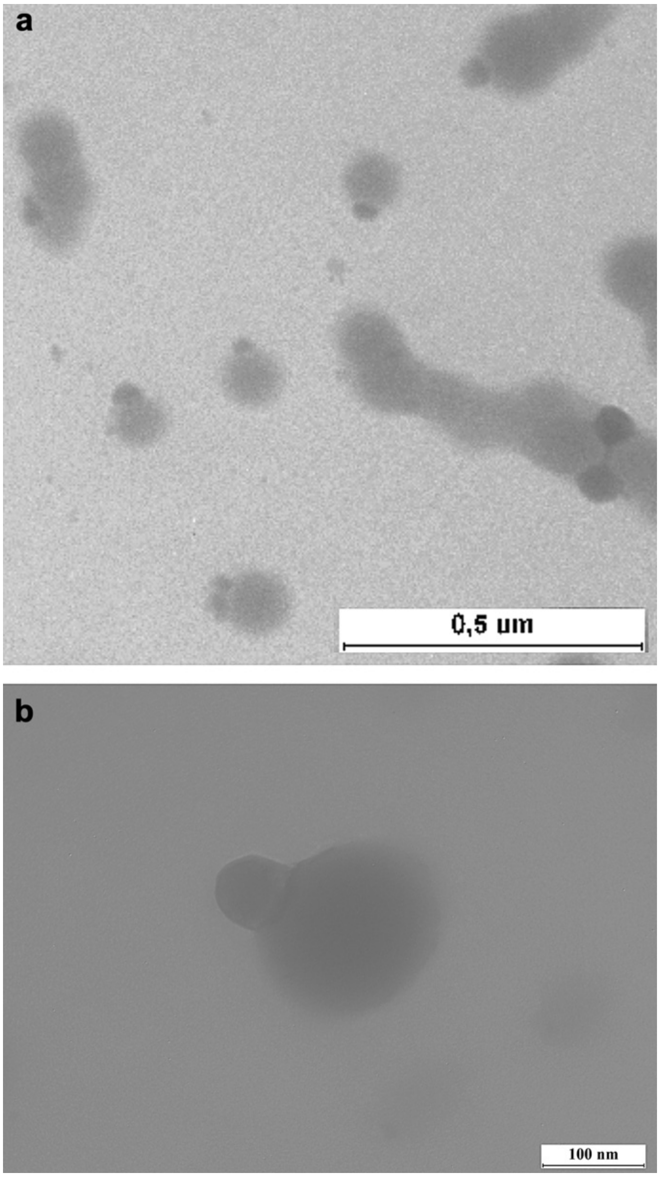

Fig. 3. TEM pictures of a poly(GMA-*co*-BMA)/poly(VDC-*co*-MA) composite latex.

Table 9
Rate constants for the dehydrochlorination of composite and reference PVDC powders at 160 °C.

Entry	Poly(GMA-*co*-BMA) content (%)	$k_{\mathrm{init}} \times 10^4$ (s^{-1})	$k_{\mathrm{prop}} \times 10^4$ (s^{-1})
C5	2.5	0.87	11.2
C3	1.7	1.33	11.3
C1	1.0	3.98	9.73
R1	0	4.72	16.9

was beneficial for the PVDC thermal stability. The impact of poly(GMA-*co*-BMA) on the polymer degradation appears to be double: it does not only inhibit the period of initiation of dehydrochlorination, but also slows down the propagation step.

On the contrary, in the case of composites obtained without TSPP, the polymer dehydrochlorination appeared to be faster than for the reference sample. This could originate from the fact that chain ends are believed to be the main defects contributing to the degradation of low molecular weight PVDC copolymers, although conflicting results were reported concerning a possible correlation between molecular weights and dehydrochlorination rates [7,27,28]. Furthermore, in this case most epoxy groups (at least 80%) were hydrolyzed during the second-stage polymerization process, and could not contribute to the polymer stabilization. Thereby both effects may have contributed to a worsened thermal stability.

To quantify the effects of epoxy-functionalized seeds on PVDC degradation, first order rate constants of initiation (k_{init}) and propagation (k_{prop}) of the polymer dehydrochlorination [9,29,30] were determined via the local slopes of $\ln((w_\infty - w_0)/(w_\infty - w_t))$ versus t, where w_0 is the initial sample weight, w_t the sample weight at a given time t and w_∞ is the sample weight at infinite time corresponding to the loss of 1 mol of HCl per VDC unit in the polymer ($w_\infty = 0.7238 \times w_0$). The values given in Table 9 confirm that the presence of epoxy-functionalized seed polymer in composite latexes resulted in slowing down the evolution of HCl during both initiation and propagation steps of the degradation process.

Two poly(GMA-*co*-BMA) latexes (S3 and S7) were mixed to the reference latex R1 so as to obtain latex blends with similar seed contents as composite latexes C5 (2.5%) and C3 (1.7%). These latex blends were then subjected to freeze-drying and resulting powders were analyzed by thermogravimetry (Fig. 5). The blends exhibited a slower degradation than the reference sample but showed a slightly shorter inhibition period than their respective composite

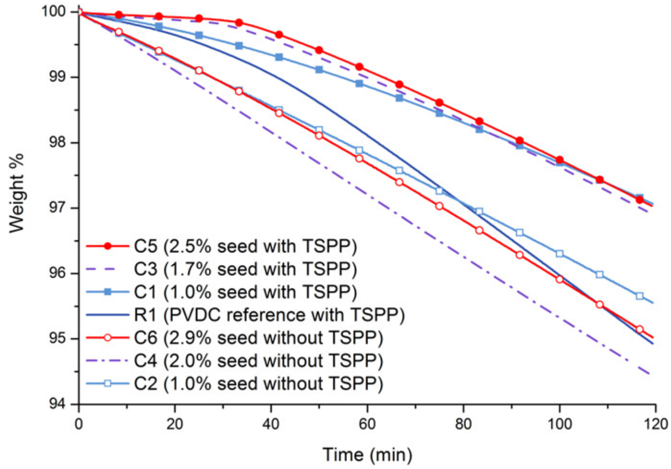

Fig. 4. Thermogravimetric analyses carried out at 160 °C for 120 min under air atmosphere for the composite particles and the reference PVDC powders.

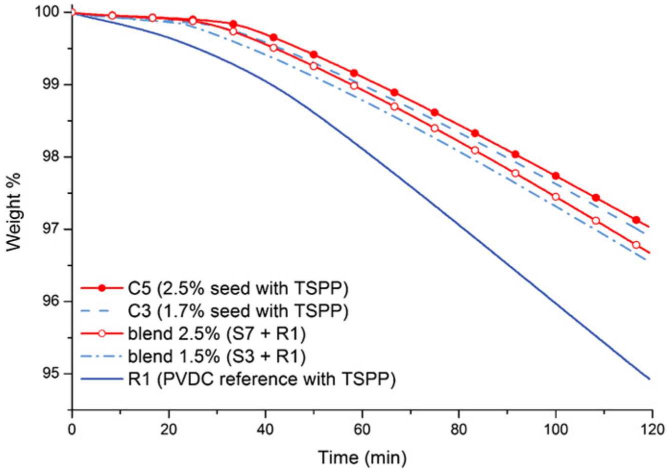

Fig. 5. Mass loss of composite, blend and reference PVDC powders versus time at 160 °C under air atmosphere.

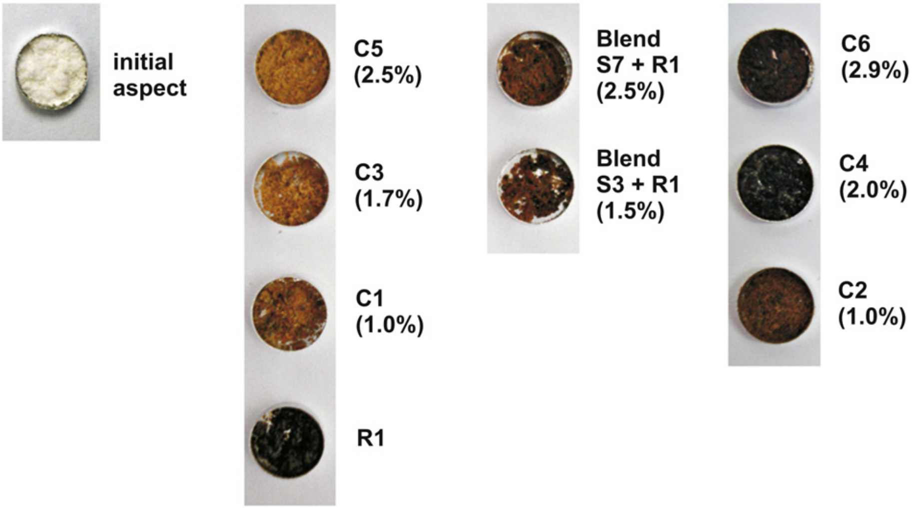

Fig. 6. Visual comparison of PVDC powders after 120 min of exposure to a temperature of 160 °C under air atmosphere.

counterparts. It brings us to the conclusion that the sample nanostructure had an impact on the polymer thermal stability. This effect may originate from the quality of the dispersion of poly(GMA-*co*-BMA) particles into the poly(VDC-*co*-MA) matrix. Blends of the two latexes may indeed result in the formation of larger poly(GMA-*co*-BMA) domains and thus HCl may be scavenged more efficiently by epoxy groups in the case of composite structures due to a more intimate contact between the two polymer phases. Along the same line, one can assume that PVDC films obtained from composite latexes will exhibit a further enhanced stability compared to reference samples, given that an even more intimate contact between the poly(GMA-*co*-BMA) seed particles and the poly(VDC-*co*-MA) matrix can be expected in film forming situations.

Pictures of the powders taken at the end of TGA analyses (Fig. 6) provided a visual confirmation of the stabilizing role of poly(GMA-*co*-BMA) seeds. PVDC coloration originates from the creation of conjugated polychloroacetylene sequences into the polymer chains upon dehydrochlorination [7]. The evolution of colour observed on degraded samples is thus in good agreement with the trends indicated by TGA experiments. These pictures also made clearly visible the better thermal stability of composites compared to their corresponding blends.

4. Conclusions

Poly(GMA-*co*-BMA)/poly(VDC-*co*-MA) composite latexes were synthesized via a two-stage emulsion polymerization process. We showed that the conditions of temperature and pH during the first-stage emulsion copolymerization of glycidyl methacrylate and butyl methacrylate affected the hydrolysis of epoxy groups, while the monomer feed rate could be adjusted in order to control the average particle diameter. Due to its role of HCl-scavenger, TSPP appeared to be a key component during the seeded second-stage emulsion copolymerization of vinylidene chloride and methyl acrylate to limit the hydrolysis of epoxy groups and obtain higher molecular weights.

Isothermal thermogravimetric analyses carried out on freeze-dried samples obtained from poly(GMA-*co*-BMA)/poly(VDC-*co*-MA) latexes showed that composites displayed an enhanced thermal stability compared to PVDC reference samples, which confirmed the role played by epoxy groups in the thermal stabilization of PVDC. These characteristics make poly(GMA-*co*-BMA)/poly(VDC-*co*-MA) latexes good candidates for use as waterborne barrier films with improved thermal stability. Work is in progress to assess the barrier properties of the resulting films and the results will be reported elsewhere.

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References

[1] Li Y, Weng Z, Pan Z. Barrier properties of vinylidene chloride/methyl acrylate copolymer. Chin J Polym Sci 1997;15(4):319–24.
[2] Delassus PT, Strandburg G, Howell BA. Flavor and aroma permeation in barrier film - the effects of high-temperature and high Humidity. Tappi J 1988;71(11):177–81.
[3] Wessling RA. Polyvinylidene chloride. In: Polymer monographs, vol. 5. Gordon and Breach Science Publishers; 1977.
[4] Wessling RA, Gibbs DS, Obi BE, Beyer DE, Delassus PT, Howell BA. Vinylidene chloride polymers. Kirk-Othmer Encycl Chem Technol 1999;25:691–745.
[5] Li YS, Pan ZR. Structure and thermal properties of vinylidene chloride/acrylics copolymers. J Appl Polym Sci 1996;61(13):2397–402.
[6] Collins S, Yoda K, Anazawa N, Birkinshaw C. The thermal stability of some vinylidene chloride copolymers. Polym Degrad Stab 1999;66(1):87–94.
[7] Howell BA. Degradation of vinylidene chloride/phenylacetylene (VDC/PA) copolymers: effect of internal unsaturation on poly(vinylidene chloride) stability. J Polym Sci Part A Polym Chem 1987;25(6):1681–95.
[8] Howell BA, Delassus PT. Degradation of vinylidene chloride/methyl acrylate/phenylacetylene (VDC/MA/PA) terpolymers: effect of internal unsaturation on the stability of Saran copolymers. J Polym Sci Part A Polym Chem 1987;25(6):1697–708.
[9] Howell BA, Ray JA. Comparison of isothermal and dynamic methods for the determination of activation energy by thermogravimetry. J Therm Anal Calorim 2006;83(1):63–6.
[10] Howell BA. Determination of the principal defect site responsible for Saran degradation using thermogravimetric Analysis. Thermochim Acta 1988;134:207–15.
[11] Howell BA, Betso SR, Meltzer JA, Smith PB, Debney MF. Thermal-degradation of epoxidized soybean oil in the presence of chlorine-containing polymers. Thermochim Acta 1990;166:207–18.
[12] Michel C, Nagels P, Francoisse P, Guenaire B. EP 500167 (Solvay); 1992.
[13] Ballistreri A, Foti S, Maravigna P, Montaudo G, Scamporrino E. Mechanism of thermal decomposition of poly(vinylidene chloride). Polymer 1981;22(1):131–2.
[14] Howell BA, Keeley JR. Decomposition of vinylidene chloride copolymers in the presence of selected transition metal halides. Thermochim Acta 1996;272:131–7.
[15] Mori S, Barth HG. Size exclusion chromatography. Springer Verlag; 1999.

[16] Revillon A, Dumont B, Guyot A. Molecular-weight determination of vinylidene-chloride copolymers by gel-permeation chromatography and viscometry. J Polym Sci Part A Polym Chem 1976;14(9):2263–73.

[17] Geurts JM, Jacobs PE, Muijs JG, van Es JJGS, German AL. Molecular mass control in methacrylic copolymer latexes containing glycidyl methacrylate. J Appl Polym Sci 1996;61(1):9–19.

[18] Cheetham PF, Tabner BJ. A spin-trap study of the peroxodisulfate-disulfite-iron initiator system. Makromol Chem Rapid Commun 1990;11(5):205–9.

[19] Smith WV, Ewart RH. Kinetics of emulsion polymerization. J Chem Phys 1948; 16(6):592–9.

[20] House DA. Kinetics and mechanism of oxidations by peroxydisulfate. Chem Rev 1962;62(3):185–203.

[21] Kolthoff IM, Miller IK. The Chemistry of persulfate .1. The kinetics and mechanism of the decomposition of the persulfate ion in aqueous medium. J Am Chem Soc 1951;73(7):3055–9.

[22] Liang CJ, Wang ZS, Bruell CJ. Influence of pH on persulfate oxidation of TCE at ambient temperatures. Chemosphere 2007;66(1):106–13.

[23] Gonzalez-Ortiz LJ, Asua JM. Development of particle morphology in emulsion polymerization. 1. Cluster dynamics. Macromolecules 1995;28(9):3135–45.

[24] Wu S. Calculation of interfacial tension in polymer systems. J Polym Sci Part C Polym Lett 1971;34(1):19–30.

[25] Kim J-W, Kim J-Y, Suh K-D. Preparation of impact modified epoxy resin by using poly(butyl acrylate)/poly (glycidyl methacrylate) core-shell composite particles. J Macromol Sci Pure Appl Chem 1998;A35(2): 249–60.

[26] Wu S. Surface and interfacial tensions of polymer Melts .2. Poly(Methyl methacrylate), Poly(Normal-butyl methacrylate), and polystyrene. J Phys Chem 1970;74(3):632–8.

[27] Burnett GM, Haldon RA, Hay JN. Dehydrochlorination of polymers. I. Poly(-vinylidene chloride). Eur Polym J 1967;3(3):449–57.

[28] Davies DH, Everett DH, Taylor DJ. Kinetics of dehydrochlorination of Poly(-Vinylidine chloride) .1. General nature of reaction and effects of temperature, molecular weight and morphology on first stage of reaction. Trans Faraday Soc 1971;67(578):382–401.

[29] Howell BA. Kinetics of the thermal dehydrochlorination of vinylidene chloride barrier polymers. J Therm Anal Calorim 2006;83(1):53–5.

[30] Howell BA. Utilization of thermogravimetry in the study of reaction mechanism. J Therm Anal Calorim 2008;93(1):27–34.