Application of Peroxide Macroinitiators in Core-Shell Technology for Coating Improvements

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Summary: New approach to synthesis of core-shell latices is proposed in the presented work. The method is based on the peroxide macroinitiators utilization for formation of the seed particles with tethered to their surface peroxide moieties. As a result, initiation and chain-growing reactions of polymerization of the shell-forming monomer are localized precisely at the seed latex interface. That allows to diminish consumption of this monomer required for complete encapsulation of a core polymer. The advantages of this new method over the conventional core-shell technology are reflected in improving the properties of polymer coating derived from such latices.

Introduction

Latices with the core-shell particle structure are of great interest for various applications. Those of them constituted by a hard polymer core like polystyrene (PS) or polymethylmethacrylate (PMMA) and a soft polymer shell, e. g. polybutylacrylate (PBA) or polybutylmethacrylate (PBMA), have excellent film-forming properties [1, 2], therefore they might be used in diverse water-borne paint formulations. Another type of latices with soft corn and hard shell has been successfully applied as impact modifiers for rigid polymers [3, 4]. In any case latices with complex particle structure are synthesized via multistage sequential emulsion polymerization of two or more diverse by nature monomers and this technology can be briefly described as follows. At the outset, the first monomer is polymerized to form latex which is further served as seeds for successive polymerization of another kind of monomer forming the polymer shell on its particles. The complexity of this process, governed by many kinetic, thermodynamic and colloidal factors, is the main reason why formation of a true core-shell structure does not always succeed [4] and obtained particles thereby might have other distinct morphologies [1, 5, 6]. Among these factors the nature of the initiator used for performing

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second stage of polymerization is of high importance [7]. In the majority of cases better results were achieved with rather water-soluble initiators, e. g. potassium or ammonium persulfates, than with oleo-soluble ones.

Another approach to synthesis of core-shell latices is proposed in the presented work. This method intends using peroxide macroinitiators for formation of the seed particles with tethered to their surface peroxide moieties. As a result, initiation and chain-growing reactions of polymerization at the second and subsequent stages of the process are localized precisely at the seed latex interface. This permits to diminish the number of factors, which strongly affect shell formation, thereby this process becomes more stable and reproducible.

Peroxide macroinitiators (PMI) are oligomer products invented and intensively developed for two past decades in Lviv Polytechnic University [8]. Their synthesis is performed via the radical copolymerization of peroxide monomers with other various functional monomers; as a result the structure of PMI can be easily tailored in a wide range aimed at involving required functionalities what is achieved by choosing the proper initial functional monomers. It is worth mentioning that a number of monomers with diverse functional groups is technically available at the present time. Moreover, the polymer modification reaction involving these functionalities allows to widen the possibility for PMI design with diverse structures and required properties. On the other hand, many peroxide monomers with different thermal stability have been synthesized as well. Thus, this method provides incorporating of the hydroperoxide, perester, or ditertiary peroxide moieties into the structure of macroinitiators. In this way the precise control of performing the free radical processes is achievable due to generation of free radicals with defined rates under chosen conditions applying either thermal decompositions of PMI or their RedOx reactions.

Concerning the functional monomers, the peroxide copolymers of (meth) acrylic acid and maleic anhydride were found to have notable features, therefore they are most often used. Due to the presence of both the hydrophilic, e.g. acid, and hydrophobic peroxide moieties in macromolecules of PMI they demonstrate surface-active properties in water solutions [8, 9] thereby they can be used as reactive surfactants for emulsion polymerization. In the last case PMI serves simultaneously as a surfactant stabilizing monomer-polymer particles and as an emulsion polymerization initiator due to decomposition of its peroxide group [8, 10]. On the other hand, so far as PMI has high tendency to adsorption at the surface of dispersed phase and is capable of initiating radical processes, it might be a useful compound for the surface modification of polymers, particularly for creation of core-shell latices.

The presented work is targeted at demonstrating the achievements gained in improving the polymer coating properties when PMI are applied in core-shell technology.

Experimental

Materials

As peroxide macroinitiator we have used oligo(5-*tert*-butylperoxy-5-methyl-1-hexen-3-in-*co*-maleic anhydride) synthesized via radical copolymerisation of peroxide monomer with maleic anhydride in acetone in the presence of lauroyl peroxide as initiator at 60 °C as described elsewhere [9].

Monomers: styrene (Merck), butylacrylate (Aldrich), ethylacrylate (Aldrich), and methylmethacrylate (Aldrich) were used for latex synthesis after vacuum distillation.

Other ingredients. Ammonium persulfate (APS, Merck) was used as initiator of emulsion polymerization. Sodium lauryl sulfate (SLS, Merck) and Dowfax 2A1 (Dow Co) were used as surfactants for latex stabilization.

Procedure

PMI immobilization on the seed particles. Core-polymer latices have been synthesized by conventional methods [11] under a nitrogen blanket in a four-neck reactor equipped with a stirrer, reflux condenser, inlets for inert gas and feeding and outlet for taking probes during the process. The control of monomer conversion was performed via estimation of non-volatile residue as well as with the aid of liquid-gas chromatography. Water solution of approximately 12 wt % of PMI was prepared in a separate flask and then different amounts of this solution were added to core-polymer latex. The mixture was stirred firstly at ambient temperature for 30 min and then at 90 °C for ca. 6 hours, afterwards the reactor was cooled.

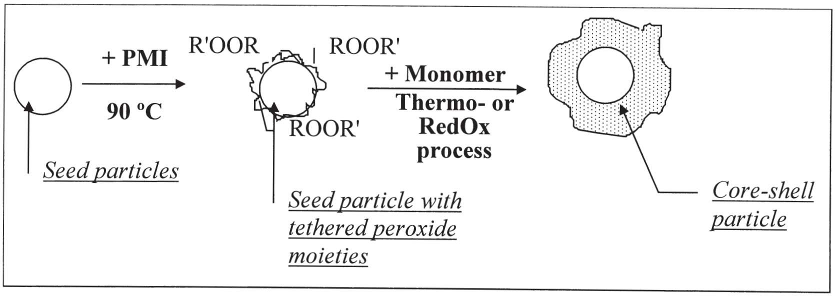
Synthesis of core-shell latex was performed in the same reactor. For that the second-stage monomer was added in a proper manner (either entirely in the beginning of the process, either by several portions or dropwise during the process). If required the components of RedOx system and additional amount of surfactant were charged as well. Thereafter the mixture was heated under continuous stirring. The monomer conversion was controlled as above.

Particles sizes were determined applying Malvern System 3000.

For obtaining the coating some amount of latex was poured on glass plate afterwards air-dried for 48 hours. The following assessments were performed to characterize the quality of latex films: adhesion was estimated in balls by conventional grid-cutting method; hardness was measured with the aid of pendulum apparatus and expressed in relative units (R.U.), whereby 100 corresponds to the glass hardness; opacity was calculated using the expression: $Opacity = \frac{D}{\Delta H}$, where D is optical density of the film and ΔH – its thickness (mm).

Results and discussions

The main idea described there consists in the following. Water solution of PMI is added to any ready-made latex and the mixture is heated at about 90 °C for several hours. As a result the PMI macromolecules are bonded to the surface of seed latex. Peroxide groups, immobilized in this way, serve further for initiating the graft-polymerization of vinyl monomer onto these particles, i.e. for forming the polymer particles with core-shell structure. This process is schematically shown below.



Scheme 1. Formation of core-shell latex particles applying PMI.

The process of PMI immobilization at seed latex particles is sufficiently complicated. It is suggested to occur via the radical mechanism and involve several elementary stages, among which the main ones are: adsorption of PMI on the particle surface; partial decomposition of PMI peroxide groups; activation of the polymer substrate surface via the chain transfer reactions; and chain termination reactions via recombination mechanism. These altogether leads to PMI coupling with the latex particle surface thereby the immobilization of the reactive peroxide groups at interface is achieved. The analysis performed with the use of different techniques (Thermo-Gravimetric Analysis, Differential Scanning Calorimetry and NMR-Spectroscopy of the latex polymer, potentiometric titration of the serum separated from frozen latex probes) proved almost complete bonding of PMI.

PS core latex particles modified with PMI in such a way have been used for synthesis of core-shell latices. Shell formation was achieved via the radical polymerization of BA initiated due to either thermal decomposition of peroxide moieties, immobilized at the core particles at 90 °C, or their decomposition facilitated by interaction with the reduction system (iron II sulfate –Chelaton B – Rongalit) at 40 °C. Figure 1 shows the kinetic curves of BA polymerization in the presence of PS core particles containing various PMI amounts.

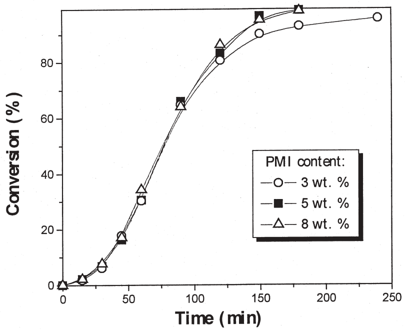


Figure 1. Kinetics of BA polymerization in the presence of PS seed particles modified with various amount of PMI.
PMI content is given in legend;
BA to PS ratio is of 3 : 10 by weight;
Temperature 90 °C.

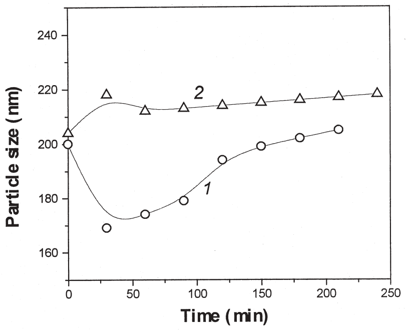


Figure 2. Time dependence of the average particle size at BA polymerization in the presence of PS core latex initiated by 3 wt. % of PSA at 84 °C (1) and by 5 wt. % of PMI immobilized at 90 °C (2).
BA to PS ratio is of 1 : 3 by weight.

As it can be concluded from the presented data the process is not practically influenced by PMI content. The possible explanation for this phenomenon could be found in the theory of emulsion polymerization [11]. One of basic statements of this theory is an assumption that any latex particles may contain only one growing radical at any time. Because of small volume of the particles appearance two or more radicals there leads to their immediate interaction, i.e. to their termination. The main conclusion drawn from this theory is the statement that the total polymerization rate is independent on the rate of initiation reaction but is strongly influenced by the number of particles. This is the reason why increase in the amount of PMI tethered to seed particles does not effect the total rate of BA polymerization. On the other hand, this is also an evidence that BA polymerization occurs on the seed particles surface but does not occur in water phase. If the latter would take place, an increase in PMI concentration should brings about the nucleation of new polymer particles, i.e. enlarge their number in the system thereby accelerating the process, what is not observed in reality. Although the PMI concentration has no effect on the rate of shell-polymerization, the core-shell latices, obtained with the use of various amount of immobilized PMI, differ in their aggregative stability, particularly against frosting (Table 1).

Table 1: Frosting effect on particle size of PS core – PBA shell latices

Amount of PMI immobilized on core particles (%)	Particle size (nm) before frosting	Particle size (nm) after frosting
3.0	202	coagulation
5.0	203	292
8.0	208	254

Improved aggregative stability of latices modified by PMI has been observed in the previous investigations [12] and was attributed to enhancement of their electro-steric stabilization. It was supposed that immobilization of PMI macromolecules brings about an increase of charge density on the particle surface as well as appearance of the steric barrier hindering coagulation. It also results in some drop of the average particle size, presumably because of deterioration of their tendency to aggregation.

Comparative investigations of changes in the average particle size (Figure 2) were performed during BA shell-polymerization initiated by PMI tethered to the PS seed particles or by water-soluble initiator PSA in accordance with [13]. It is evident from Figure 2 that topochemistry of these processes is appreciably distinct.

Decomposition of PSA in aqueous phase brings about homogeneous nucleation of the number of small PBA particles at the initial stage of the process, what is indicated by sharp drop in the average particle size (Figure 2, curve 1). Because the adsorption layers of newly formed particles are strongly unsaturated they have strong tendency to coalescence, first of all at the surface of core particles which are essentially larger. Since this occurred the polymerization process takes place on the core-shell particle surface (particle size growth section of curve 1).

The topochemistry of shell formation involving PMI immobilized is essentially different. From the beginning of the process, BA polymerization occurs on the surface of PS particles, where the initiation sites are localized. Curve 2 in Figure 2 confirms the absence of homogeneous nucleation of PBA particles in this case, since the particle size is rising already at the initial stage of the process.

So, obtaining of core-shell latices with the use of PMI immobilized has some advantages over the conventional technique applying water-soluble initiators. Above all this concerns more effective utilization of shell-forming monomer. Because of its partial consumption in the process of homopolymer particle formation as described above, the core-shell latices obtained applying conventional technique demonstrate the film-forming properties at the weight ratio of core- to shell-polymers ranging from 1 : 1 to 1 : 9.

On the contrary, the proposed technique allows the localization of shell-monomer polymerization exactly at the surface of seed particles thereby diminishing its consumption required for complete covering core-polymer. Moreover, this is a case when the highest ratio of hard core- to soft shell-polymers, at which the latex possesses the film-forming properties, can be easily predicted on the basis of consideration the film formation process. Films derived from core-shell latices are typical heterogeneous materials, where the shell polymer serves as the continuous phase within which the core-polymer particles are distributed. The model of maximal packing predicts in the case of uniform spherical undistorted particles their highest volume partition to be of 0.67. In the case of polydisperse particles this value might however rise up to 0.77. In this model soft polymer just simply fills the space between those particles. On the other hand, one should bear in mind that the hard particles have to be completely encapsulated by soft polymer in order to achieve formation of a tight film, i.e. correction ought to be made on the thickness of shell layer. Assuming this thickness should be not less than 10…20 % relative to the core particle size, it is easy to estimate the required ratio to be in the range of 3 : 1 to 2 : 1.

Series of latices with various PS core to PBA shell ratios were synthesized applying both the conventional and new techniques in order to evaluate their efficiencies. With this purpose latex films of about 0.3 mm thickness, cast on the glass plates, were examined on adhesion, hardness and opacity (Table 2). For comparison there are given the properties of film derived from commercial vinyl-acrylic latex AC-264 widely used in water-borne paint formulation.

Table 2. Composition of latex dispersion and properties of film

		Latex properties		Film properties		
No	Technique used for obtaining latex dispersion	PS to PBA ratio	Particle size (nm)	Adhesion (ball)	Hardness (R.U.)	Opacity (mm^{-1})
1	New core-shell with PMI use	3 : 1	216	0	47.4	3.12
2	New core-shell with PMI use	2 : 1	210	0	41.6	2.69
3	Conventional core-shell with PSA use	3 : 1	198	2	–	–
4	Conventional core-shell with PSA use	1 : 1	208	0	24.8	2.87
5	Blend of homopolymer latices	1 : 1	201	2	31.4	2.99
6	Commercial vinyl-acrylate latex AC-264		206	0	15.7	0.17

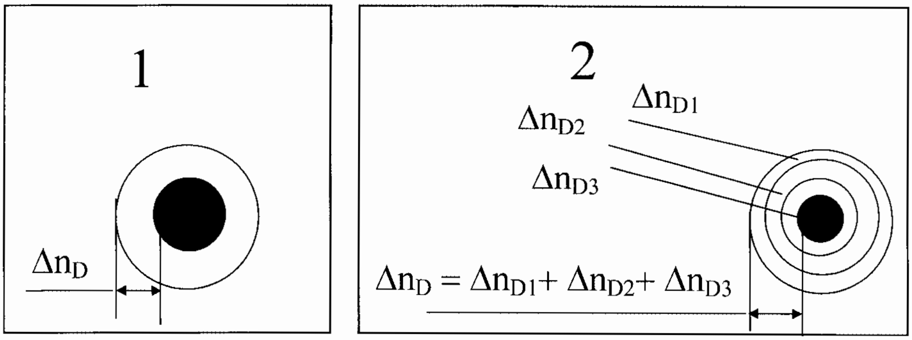
Evident is the fact that the adhesion of core-shell latices obtained using PMI even at low content of PBA is similar to that of commercial latex. Applying conventional method for obtaining the core-shell latices a similar result is achieved at higher content of PBA. At least equal amounts of the core- and shell-polymers are required in this case. Plain blending of two homopolymer latices does not give acceptable results. Another distinct properties of the films derived from the newly synthesized core-shell latices is their essentially higher hardness (2…3 times) than that of the other latex films. This is an important result because low hardness usually attributed to latex coating is one of the main obstacles that hinders their wide application in paint formulations.

Film opacity is only one position where new latices lose to commercial product substantially. This is because the core-shell latices are capable of forming only heterophase films what is the result of thermodynamic incompatibility of the core- and shell-polymers. The high difference in their refractive indexes (n_D) causes light scattering on their phase boundaries, therefore such films cannot be as highly transparent as those formed by the latex with homophase particles.

There are two approaches to enhance transparency of the films formed by heterophase particles:

- choice of the core- and shell-polymers with as much as possible close or better with equal refractive indexes;
- creation of multilayered particles with a radial gradient of refractive index.

If the first of these approaches is clear, the second one requires some comments to be made. The graphic interpretation of the last approach is given in Scheme 2.



Scheme 2. Structure of plain core-shell (1) and multilayered (2) latex particles.

There every two neighboring layers do not differ in n_D as much therefore such particles as well as the material formed from them have a vague phase boundary, consequently slight scattering properties. In practice this might be realized via gradual changes in the content of copolymers forming each of these layers. Tables 3 and 4 show the receipts of multilayered core-shell latices synthesized with the use of PMI and film properties derived from them. There are appreciable gains in the transparency of the films while other characteristics are similar to those of previous latices (Table 2).

Table 3. Composition and properties of multilayered core-shell latices

	Core composition (%)					1^{-st} shell composition (%)			2^{-d} shell composition (%)		Latex properties	
No	S	BA	BMA	MMA	PMI	S	BA	BMA	BA	BMA	NVR (%)[*]	Particle size (nm)
7	30	-	3	3	2	20		19	23	-	46.5	209
8	30	-	3	3	2	20		19	-	23	39.4	197
9	30	3	-	-	2	20	3	19	23	-	40.9	213
10	30	3	-	3	2	17	3	19	-	23	42.5	192
11	30	3	3	-	2	17	3	19	23	-	42.0	202

[*] – non-volatile residue.

Table 4. Properties of the films derived from multilayered core-shell latices

No	ΔH (mm)[*]	Adhesion (ball)	Hardness (R.U.)	Opacity (mm^{-1})
7	0.24	0	61	1.53
8	0.25	0	60	1.84
9	0.24	0	60	1.79
10	0.26	0	52	1.52
11	0.30	0	54	1.53

[*] – film thickness.

To prove the first approach to obtaining transparent heterophase coatings the core-shell latices have been synthesized with the use of PMMA as core-polymer ($n_D = 1.485$) and PBMA ($n_D = 1.483$) or some BMA copolymers with methacrylic acid (MAA) or ethyl acrylate (EA). The results are given in Table 5.

Table 5. Properties of the films derived from core-shell latices with MMA core-polymer

		Latex properties		Film properties		
No	Shell-monomer composition (%)[*]	NVR (%)	Particle size (nm)	Adhesion (ball)	Hardness (R.U.)	Opacity (mm^{-1})
12	BMA (50)	42.7	226	0	51.6	0.60
13	BMA (45); MAA (5)	51.8	224	0	50.8	0.42
14	EA (23); BMA (27)	40.0	208	0	41.3	0.14
15	MMA (48); EA (25); BMA (27)	41.1	212	1	34.0	0.26

[*] The monomer percentage is based on core-polymer weight.

Analyzing these data one can conclude that application of PMI in the core-shell technology allows to obtain the latices with the film-forming properties which are similar to those of vinyl-acrylate latex but exceeding the latter in the coating hardness.

Conclusions

As a result of the investigations performed a new approach to synthesis of core-shell latices has been developed. It is based on the peroxide macroinitiators utilization for formation of the seed particles with tethered to their surface peroxide moieties. As a result, initiation and chain-growing reactions of the shell-polymerization are localized precisely at the seed latex interface. This allows to diminish consumption of shell-forming monomer required for complete encapsulation of a core polymer thereby improving the properties of polymer coating derived from such latices.

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