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Designing tubular reactors to avoid clogging in high solids miniemulsion photopolymerization

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HIGHLIGHTS

- High solids miniemulsion photopolymerization in a continuous tubular reactor.
- Reasons for occurrence of reactor clogging are unveiled.
- Facile test to predict which miniemulsions lead to tubular reactor clogging proposed.
- Reactor design to overcome clogging is presented.

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ABSTRACT

Tubular reactors are attractive for the synthesis of complex waterborne dispersed polymers by photoinitiated miniemulsion polymerization. However, tubular reactors are not yet used in commercial production of emulsion polymers mainly because they are prone to suffer clogging. In this work, the reasons for the occurrence of tubular reactor clogging in high solids miniemulsion photopolymerization are unveiled, a facile test to predict if a given miniemulsion will lead to clogging in the tubular reactor is proposed, and a reactor design to overcome clogging is presented.

1. Introduction

Miniemulsion polymerization [1] is the method of choice for the synthesis of complex dispersed polymers [2–4]. Commonly, miniemulsion polymerization involves a free radical polymerization initiated by redox or thermal initiators. This limits the range of temperatures that can be used, because the polymerization suffers from irreproducibility at low temperatures [5,6]. In some cases, it is desirable to perform the polymerization at low temperatures. Thus, ultrahigh molecular weights [7] and coatings with improved scrub resistance [5] have been produced at low temperatures. In addition, polymerization temperature strongly affects the polymer architecture of polyacrylates, which are often used for waterborne coatings and adhesives. The reason is that inter and intramolecular transfer to polymer shape the chain architecture of the polyacrylates and as the activation energies of these reactions are substantially higher than that of the propagation ($E_{tpintra}$ = 29.3 kJ/mol; $E_{tpinter}$ = 27.7 kJ/mol; E_p = 17.9 kJ/mol) [8–11], the number of short and long branches (and hence gel) are expected to decrease for low temperatures. For all these systems, the limits in the workable polymerization temperature restrict the range of attainable polymer architectures.

Photopolymerization provides a fast generation of radicals even at low temperatures, and is a useful alternative to thermally induced polymerization. In order to implement photoinitiated miniemulsion polymerization at low temperatures, it is necessary to overcome some challenges. On one hand, strong light scattering occurs in the waterborne dispersed polymers, and hence the penetration depth of the irradiation is low and stirred tank reactors cannot be efficiently used [12,13]. On the other hand, in polymerization in dispersed media, production is limited by the heat removal rate [14] that is proportional to the temperature gradient between the reactor and the cooling fluid. As economic reasons limit the minimum value of the temperature of the cooling fluid,

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the heat removal per unit area decreases as the reactor temperature decreases, namely, production decreases.

Tubular reactors can overcome these limitations because, due to their large surface area/volume ratio, a large part of the reaction mixture can be irradiated even with modest penetration depths and the polymerization heat is efficiently removed at low reactor temperatures.

Tubular reactors are not free from problems. Actually, except for the loop reactor [15], they are not yet used in the commercial production of emulsion polymers. Their main drawback is that they are prone to suffer coagulations and lack of reproducibility. Coagulation is mostly due to gravity induced phase separation (creaming) and special reactor designs have been proposed to avoid this problem by modifying the flow pattern in the reactor [16]. Irreproducibility results from random variations of the inhibitor content in the feed that propagate through the tubular reactor. Technical monomers (i.e., containing inhibitors) are used in commercial practice. Even for the same supplier, the inhibitor concentration is not a precise value, but a range of concentrations. In addition, the concentration of oxygen, which acts as an inhibitor, in the monomer is difficult to control. The result is that the total concentration of inhibitor can vary considerably. In the polymerization, monomer and inhibitor compete for radicals and hence and induction period in which the polymerization rate continuously increases is usually observed. This induction period is very sensitive to the total concentration of inhibitor. In a tubular reactor that works at constant residence time, the varying inhibition period results in a varying monomer conversion at the exit of the reactor.

We have recently reported the use of a quartz tubular reactor for the synthesis of PU-acrylic pressure sensitive adhesives (PSAs) by miniemulsion photopolymerization [17]. Quartz is used because it is transparent to the UV radiation. The process ran smoothly without coagulation problems, which was attributed to the high stability of the miniemulsion. In addition, the process was reproducible, even though technical monomers (i.e., containing inhibitors) were used. The reason was that a high flux of radicals was produced. That work demonstrated the potential of miniemulsion photopolymerization in tubular reactors to synthesize complex materials as well as the flexibility of the process to control the polymer architecture that could be strongly varied by simply modifying the photoinitiator (PI) concentration and the incident light irradiance (ILI).

However, in that work, 20 wt% solids content was used, which is too low for a commercial latex. Therefore, we decided to increase the solids content to 45 wt% using the formulation given in Table 1, but in all the attempts, coagulum was formed and the reactor was clogged after running the process for some time (0.5–2 h). This was unexpected because this type of miniemulsion was smoothly polymerized in a stirred tank reactor without formation of coagulum [18]. Obviously, this problem should be overcome in order to make the process viable.

In this work, the reasons for the occurrence of clogging are unveiled, a facile test to check if a given miniemulsion will lead to clogging in the tubular reactor is proposed, and a reactor design to overcome clogging is presented.

2. Experimental

2.1. Materials

Technical grade monomers, 2-ethylhexyl acrylate (2-EHA, Quimidroga), methyl methacrylate (MMA, Quimidroga), methacrylic acid (MAA, Aldrich), 2-hydroxyethyl methacrylate (HEMA, Fluka), styrene (S, Quimidroga) and butyl acrylate (BA, Quimidroga) were used as received. N-octadecyl acrylate (SA, Aldrich) was utilized as a reactive costabilizer in order to prevent Ostwald ripening [19,20]. A polyether and aliphatic isocyanate terminated polyurethane prepolymer, Incorez 701 (PU, Incorez Ltd.), specially designed for adhesive applications, was used without further purification. The equivalent weight of the prepolymer is 1050 g/equivalent and the NCO concentration is ca. 4 mol%. Bisphenol A (BPA, Aldrich) was used as chain extender. Dibutyltin dilaurate (Aldrich) was utilized as polyaddition catalyst without any purification. Dowfax 2A1, (alkyl diphenyloxide disulfonate, Dow Chemicals) was used as surfactant to prepare the miniemulsions, sodium dodecyl sulphate (SDS, Aldrich) was added after the miniemulsification to improve the miniemulsion stability, Aerosol A-102 (CYTEC Industries BV) and Triton X-100 (Sigma) were used to prepare the aqueous solutions of surfactant. All surfactants were used as received. The non-bleaching oil soluble photoinitiator 1-hydroxycyclohexyl phenyl ketone (HCPK, Aldrich) was used as received. Sodium bicarbonate ($NaHCO_3$, Aldrich) was used as a buffer. Oxygen-free grade nitrogen was used for purging the feed. Double deionized water (DDI) was used throughout this study.

Table 1
Formulations of the miniemulsions used in the study.

45 wt% solids content PU/Acrylics miniemulsion			45 wt% solids content S/BA miniemulsion		
Component	Amount (g)	Weight (%)	Component	Amount (g)	Weight (%)
2EHA	196.43	91.5[a]	S	75	50[a]
SA	12.5	5.8[a]	BA	75	50[a]
MMA	3.04	1.4[a]	SA	9	6[a]
MAA	2.03	0.9[a]			
HEMA	1.01	0.4[a]			
PU	22.5	10[b]			
BPA	4	OH/NCO = 2[e]			
DBTDL	0.11	500 ppm[c]			
PI	0.202–1.01	0.09–0.48[a]	PI	0.75	0.5
DDI-water	270.05	–	DDI-water	179.7	–
Dowfax 2A1	9	2 (45 wt% active)[b]	Dowfax 2A1	6.66	2(45 wt% active)[a]
$NaHCO_3$	0.46	0.02 M[d]	$NaHCO_3$	0.8	0.05 M[d]
SDS	2.25	1[b,f]			

[a] Weight based on monomer weight (wbm).
[b] Weight based on organic weight (wbm).
[c] ppm based on organic phase.
[d] Based on water phase.
[e] Amount to have OH/NCO = 2.
[f] Post miniemulsification addition to improve stability.