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Semicontinuous Emulsion Copolymerization of Vinyl Acetate and Butyl Acrylate Using Different Initiators and Different Chain Length Emulsifiers

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Summary: The semicontinuous emulsion copolymerization of vinyl acetate and butyl acrylate (VAc/BuA) (85:15) initiated by thermal initiators ammonium persulfate (APS) and potassium persulfate (PPS) at 70°C in the presence of nonylphenol ethoxylates of varying chain lengths (NP-n) and acrylamide partially polymerized (Amol) was investigated. VAc-BuA copolymer latexes were synthesized as two different series in the glass reactor, in the first serie was initiated by APS and PPS was used as initiator in the second serie. The influence of the counterions or initiators and chain lenghts of non-ionic emulsifier on the properties of VAc-BuA copolymer latexes were determined by measuring Brookfield viscosities, weight average molecular weights ($\overline{M}_w$), number average molecular weights ($\overline{M}_n$), molecular weight distribution and surface tension of latexes to air. The results of copolymer latexes indicated that their physicochemical properties increased with the increasing chain length of nonionic emulsifier for two initiators.

Keywords: core-shell polymers; emulsion polymerization; initiators; non-ionic emulsifier; vinyl acetate

Introduction

Emulsion copolymers of vinyl acetate are generally water based, milky-white liquids containing 48-55 % solids, the balance being water and small amounts of emulsifiers or emulsifier mixture, protective colloids or free and other additives. Vinyl acetate (VAc) can be copolymerized with many monomers especially butyl acrylate (BuA)[1-23], 2-ethyl hexyl acrylate, Veova 10, methyl metacrylate etc. by applying different monomer compositions and using bulk, suspension and emulsion polymerization methods.[1-4] Among them, the most preferred is VAc-BuA monomer

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couple (due to their superior product properties) and the commonly used method for copolymerization is emulsion polymerization.[4] VAc-acrylic copolymer latexes and polyvinyl acetate (PVAc) are generally used as binders in water-based interior and exterior architectural paints, coatings, and adhesives, since they have higher mechanical and water resistance properties than the homopolymers of both monomers.

The studies are very limited about VAc-BuA copolymerization in the presence of protective colloids, such as polyvinyl alcohol (PVOH)[5], hydroxyethyl cellulose (HEC), and dealing with the use of nonionic emulsifiers for latex stabilization. In general, particle stabilization is achieved by the use of either nonionic or the combination of nonionic and anionic emulsifiers, which are widely employed in emulsion polymerization systems. VAc-co-BuA latex particles produced in batch reactors can have a core-shell structure. Moreover particles having this type of morphology are difficult to stabilize due to poor emulsifier adsorption characteristics of the hydrophilic VAc surface. This problem appears even with the production of homogeneous particles in semicontinuous reactors and has led to the improvement of alternating stabilization methods or agents. These include the use of functional comonomers (acrylic acid, etc.), the use of steric stabilizers (PVOH, HEC, PEG, etc.), and polymerizable surfactants.[22]

In the present work, the emulsion copolymerization system containing VAc, BuA, APS or PPS, Amol, nonyl phenol ethoxylate (NP-n) (where n designates the average chain length of the ethoxylate chain), $NaHCO_3$ and water was studied in the glass reactor. The effects of counterions, the chain lengths of EO in the emulsifier and novel protective colloid (Amol) on the physicochemical properties of obtained VAc-co-BuA latex properties were investigated. Because, a number literature can be found on the VAc-BuA emulsion copolymerization started with the same kinds of initiators[23] and different stabilizing agent except PVOH or HEC.

Experimental Part

General Method and Materials

Vinyl acetate-co-butyl acrylate latexes were synthesized in the presence of non-ionic emulsifiers which have different chain length, new protective colloid (Amol) and different initiators (ammonium persulfate and potassium persulfate). Vinyl acetate/butyl acrylate monomer ratio was determined as 85/15 based on previous studies.[4, 23-24]

In this study, copolymerizations were done in a classical glass reactor using semicontinuous feeding technique at the constant stirring rate (200 rpm) and all chemicals were used as received. Two latex series were synthesized employing different chain length of non-ionic emulsifiers; in the first series ammonium persulfate was used as initiator, and potassium persulfate was used as initiator in synthesizing of the second series copolymers.

Argon Chemistry Inc. VAc and BuA monomers were used at commercial purification and monomer ratio was 85:15. The stability of the latexes was achieved by a series of nonyl phenol ethoxylate (NP 10, 10+30, 30, 40) (Turkish-Henkel Chemicals Industry Co.) Acryl amide partially polymerized (Amol) (Elsan Fibre Co.) was used as protective colloid, ammonium persulfate (APS) (Merck) and potassium persulfate (PPS) (Merck) were used as thermal initiators, Nopco-1497 was used as an antifoam agent, and sodium bicarbonate (Merck) was used for adjusting the pH value of the polymerization media. All substances were used without further purification. De-ionized water was used in all studies. The general copolymerization recipe was given in Table 1.

Table 1. Recipes used in copolymerization experiments

Substance	% Weight
VAc	42.50
BuA	7.50
Amol	2.00
NP-n (n =10-40)	0.80
APS or PPS	0.20
$NaHCO_3$	0.12
Nopco-1497	0.10
Water	46.29
Total	100.00

Measurements

Copolymer latexes were characterized by measuring Brookfield viscosity, molecular weights ($\overline{M}_n$, $\overline{M}_w$) and surface tension of copolymer latexes to air. Conversion was monitored gravimetrically. The viscosities of the latexes were determined by Brookfield Programmable DV-II model viscometer with spindle number 4 at 26°C after diluting 40% (wt.) solids content of all samples. Number average molecular weights ($\overline{M}_n$) and weight average molecular weights ($\overline{M}_w$) of copolymers were determined by the GPC Agilent model 1100 type instrument with a refractive index detector and calibrated with polystyrene standarts consist of three Waters styragel colums (HR 4, HR 3, and HR 2). THF was diluent solvent at a flow rate of 0.3 mL/min at 30°C. The surface tensions of the produced latexes were measured after the total solids contents of the samples were adjusted to 25 % by weight by diluting. The surface tension measurements were done with ring-detachment method by torsion tensiometer and a platinium ring at 25°C.

Results and Discussion

Viscosity

The copolymer viscosities in general were slightly higher in the case APS initiator than PPS. Increasing poly(EO) block length caused to increase in the viscosities of copolymer latexes for two initiators (Figure 1.). Latexes usually show Newtonian fluid behaviour and surface layers can significantly increase the effective volume of latex particles.[1] Such layers may be due to the adsorbed surfactants, adsorbed or reacted polymeric stabilizers such as PVOH, HEC or poly(EO), and surface charges on the polymer particle. The smaller the particle size, the greater will be the contribution of a surface layer of given thickness to the effective volume of the particle. The greater viscosity, the greater will be the contribution of a surface layer of given thickness to the effective volume of the particle. That effect could be explain that the viscosity depends on an effective particle volume which increases with increasing poly(EO) block length. In addition, it is thought that VAc-co-BuA latexes show that core-shell structure, so core-shell type structure can cause to increase the viscosities of VAc-co-BuA latex.

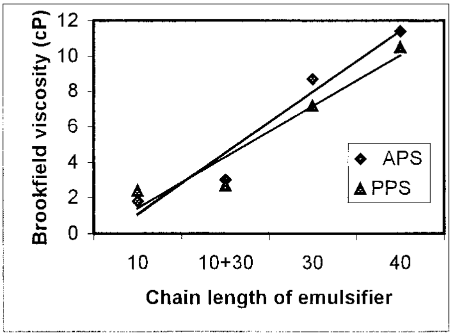
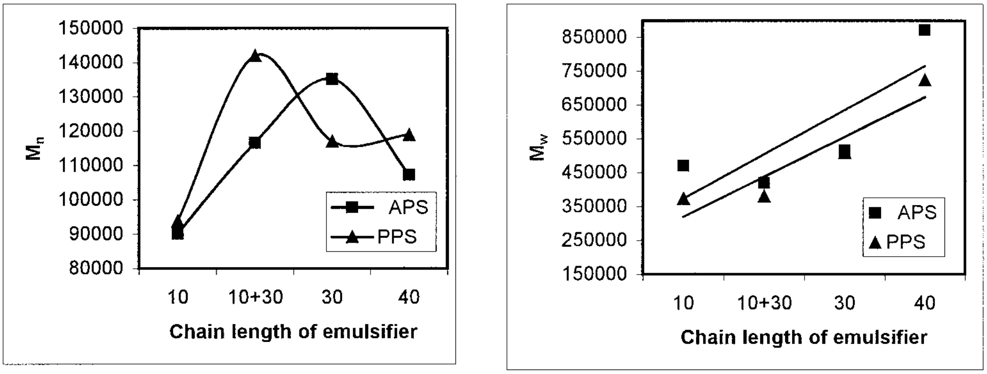


Figure 1. Change of Brookfield viscosity of copolymers versus chain length of emulsifier

Molecular weights of the copolymers

$\overline{M}_w$ and $\overline{M}_n$ of molecular weights of the poly(VAc-co-BuA) copolymers were determined by GPC. In Figure 2a. and Figure 2b. it was seen that $\overline{M}_n$ and $\overline{M}_w$ molecular weights increased by increasing the ethoxylation number of the participating emulsifiers increased for both initiator. As a result of determining of $\overline{M}_n$ VAc-BuA copolymers, PPS gave having slightly higher molecular weight copolymers than APS. Moreover either $\overline{M}_n$ or $\overline{M}_w$ of copolymers increased with increasing ethoxylation degree of emulsifier, and monodisperse copolymers (HI= 2.68-8.14) obtained by using different initiators and nonionic emulsifier with different chain lengths for two initiators. El-Aasser et. al[2] found the similar results for molecular weighs of copolymers having 85/15 monomer ratio for batch process, but obtained copolymers in this work has highly smaller polydispersity value than El-Aasser et. al.



a. b.

Figure 2.a. Change of number average of molecular weights of copolymers versus chain length of emulsifier. b. Change of weight average of molecular weights of copolymers versus chain length of emulsifier

Surface properties of the latexes

It was determined that the surface tensions of the copolymers increased with increasing chain length of nonionic emulsifier. Generally surface tensions of copolymers obtained by using same chain length of emulsifier were found almost same for two initiators (Table 2.). Because of the adsorption non-ionic emulsifier at the latex surface, surface tensions of samples were found as 38-47 mN/m.

Table 2. Surface tensions of copolymers (mN/m)

	Chain length of emulsifier			
Initiator	10	10+30	30	40
APS	38.7	39.9	45.5	46.1
PPS	39.0	40.5	45.7	46.7

Conclusion

VAc-co-BuA latexes were synthesized by using APS or PPS thermal initiators, partially polymerized acrylamide (Amol) and non-ionic emulsifiers which were different chain lengths. A comparison of the some physicochemical characteristics of VAc-BuA copolymers latexes were stabilized by nonylphenol ethoxylate molecules with varying chain lengths and Amol was presented. The viscosities of copolymer latexes, $\overline{M}_n$, $\overline{M}_w$ and surface tensions of the copolymer latexes in aqueous phase were followed same trend, and those parameters of the copolymers increased with increasing chain length of emulsifier for both initiators.

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