EFFECT OF CHAIN TRANSFER AGENT IN PRESENCE OF REACTIVE SURFACTANTS DURING SCALE-UP OF EMULSION POLYMERIZATION

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Introduction

Acrylic emulsions are a popular choice in the production of pressure-sensitive adhesives (PSAs) due to their outstanding adhesion properties, transparency, and durability. Their use offers numerous advantages, such as consistent and stable dispersion of adhesive polymers in water, ensuring uniform PSA coating. Additionally, they provide versatile PSAs with varying properties suitable for diverse applications, from labels to automotive industries. Emulsions are an environmentally friendly, water-based system with lower volatile organic compounds (VOCs), thus emitting fewer pollutants and presenting reduced health risks. They also offer easy handling, storage, and lower raw material costs, making them a cost-effective solution for many manufacturers.

Alkylphenol ethoxylates (APEs) surfactants are widely used in industrial applications, including detergents, cleaners, and emulsifiers. However, due to their persistence in the environment and potential to disrupt hormonal systems, they pose risks to human health and the environment. Consequently, there is a growing shift towards APE-free surfactants, which utilize alternative, environmentally friendly, and safer ingredients. APE-free surfactants, which encompass nonionic, anionic, cationic, and amphoteric types, are increasingly employed in consumer and industrial products, such as personal care items, cleaning products, oil and gas production, food processing, and agriculture. This transition aids in reducing the industries' environmental impact while promoting human health and safety.

Surfactants play a vital role in emulsion polymerization by stabilizing the emulsion and preventing polymer particle aggregation. As APE-containing surfactants like nonylphenol ethoxylate (NPE) and octylphenol ethoxylate (OPE) pose environmental and health risks, APE-free alternatives are gaining popularity. These alternatives include nonionic, anionic, cationic, and amphoteric surfactants, with nonionic surfactants being preferred for their compatibility with various monomers and emulsion stability. Common APE-free surfactants in emulsion polymerization are polyethylene oxide (PEO) surfactants, alkyl polyglucosides (APGs), and sodium lauryl sulfate (SLS). By using APE-free surfactants, manufacturers can reduce the environmental impact of emulsion polymerization while promoting human health and safety (1-3).

Reactive APE-free surfactants, which contain functional groups that react with monomers during emulsion polymerization, form covalent bonds with polymer chains, enhancing the stability and performance of the resulting polymer dispersions. Common reactive APE-free surfactants used in emulsion polymerization are Vinyl acetate/ethylene (VAE) copolymer-based surfactants: These surfactants, containing reactive vinyl groups that copolymerize with monomers, are often employed in producing acrylic and vinyl acetate polymer dispersions.

Glycidyl methacrylate (GMA) modified surfactants: Containing reactive epoxy groups that form covalent bonds with polymer chains during emulsion polymerization, GMA modified surfactants are frequently utilized in creating styrene-acrylic and styrene-butadiene polymer dispersions. Maleic anhydride (MA) modified surfactants: These surfactants possess reactive maleic anhydride groups that react with monomers during emulsion polymerization to form covalent bonds with polymer chains. MA modified surfactants are commonly used in producing styrene-acrylic and vinyl acetate polymer dispersions. There are commercially available reactive nonionic and anionic surfactants;

Ethers: Polyoxyethylene alkylphenyl ethers, Allyl methoxy triethylene glycol ether
Sulfonates: Sodium allyloxy hydroxypropyl sulfonates, Sodium methallyl sulfonates, AllylsulfoSuccinate derivatives
Acrylates: Sulfopropyl acrylate, Sorbitol acrylate, Phenoxyl poly(ethyleneoxy)acrylate, Nonyl phenoxy poly(ethyleneoxy)acrylate
Methacrylates: Sorbitol methacrylate, Perfluoroheptoxy poly(propyloxy) methacrylate, Phenoxyl poly(ethyleneoxy)methacrylate, Nonylphenoxy poly(ethyleneoxy)methacrylate
Maleates: Monosodium ethylsulfonate monododecyl maleate, Mono dodecyl maleate
Others: Alkenyl-functional nonionic Surfimers, Vinyl sulfonate, Vinyl phosphate, Nonyl phenoxy poly(ethyleneoxy)crotanate, Nonylphenoxy poly(ethyleneoxy)fumarate. (4-5).

Reactive APE-free surfactants provide several benefits in emulsion polymerization, including improved emulsion stability, reduced surfactant levels, and enhanced polymer properties such as adhesion, abrasion resistance, and water resistance. However, their application can be more intricate and may necessitate meticulous optimization of formulation and process conditions for optimal results.

We used commercially available APE-free reactive surfactant commonly used in emulsion polymerization in our research. Based on a vinyl ester of a fatty acid, it offers excellent emulsification and stabilization properties. Its benefits include improved emulsion stability, reduced surfactant levels, enhanced polymer properties such as adhesion, abrasion resistance, and water resistance, and being environmentally friendly by not containing alkylphenol ethoxylates.

Experimental

Polymer Design for PSA

Acrylic emulsions being widely used as the base material for pressure-sensitive adhesives (PSAs) due to their excellent properties such as good adhesion, high tack, and shear strength. While selecting the right acrylic emulsion for a specific PSA application following factors were taken into consideration.

Polymer Composition

The composition of the acrylic polymer is one of the most important factors to consider when selecting an acrylic emulsion for PSA applications. The monomers used in the acrylic polymer can affect the adhesive properties of the resulting PSA. Butyl acrylate (BA) is a commonly used monomer in PSA formulations due to its good adhesion properties. Other monomers such as methyl methacrylate (MMA), 2-ethylhexyl acrylate (2-EHA), and acrylic acid

(AA) were also used to tailor the properties of the acrylic polymer. The choice of monomers was based on the specific requirements of the PSA application.

Glass Transition Temperature (Tg*)*

The Tg of the acrylic polymer can affect the tack and shear properties of the PSA. The Tg is the temperature at which the polymer transitions from a glassy state to a rubbery state. Lower Tg values generally lead to better tack, while higher Tg values can provide better shear strength. The Tg of the acrylic polymer can also be controlled by adjusting the monomer composition and molecular weight. For the particular application, lower Tg was targeted that required good adhesion to low-energy substrates.

Particle Size and Distribution

The particle size of the acrylic emulsion can affect the coating and drying properties of the PSA. Smaller particle sizes generally provide better coating properties, while larger particle sizes can provide better shear strength. The particle size can be controlled by adjusting the surfactant type and concentration, as well as the polymerization conditions. A smaller particle size is preferred for applications that require a smooth and uniform coating, while a larger particle size is preferred for applications that require high shear strength.

Molecular Weight & Polymer Dispersity Index (PDI)

The molecular weight of the acrylic polymer can affect the viscosity and performance properties of the PSA. The molecular weight can be controlled by adjusting the monomer composition and polymerization conditions. A higher molecular weight is preferred for applications that require high shear strength, while a lower molecular weight is preferred for applications that require good coating properties. Polymer dispersity index (PDI) is a measure of the molecular weight distribution of a polymer. A low PDI indicates a narrow distribution of molecular weights, while a high PDI indicates a wide distribution of molecular weights. The molecular weight distribution of the polymer can have a significant effect on the adhesive properties of the PSA. A narrow molecular weight distribution, can provide a more consistent and uniform adhesive performance. This is because the PSA properties, such as tack and shear strength, are determined by the molecular weight of the polymer. A low PDI can provide a more uniform distribution of molecular weights, which can lead to more consistent adhesive properties. This is because a narrow molecular weight distribution ensures that the PSA is composed of a consistent population of polymer chains with similar molecular weights. In contrast, a high PDI can result in a wide distribution of molecular weights within the polymer, which can lead to a less consistent adhesive performance. This is because the PSA properties can vary significantly depending on the molecular weight of the polymer chains. A wide distribution of molecular weights can result in a population of polymer chains with significantly different molecular weights, which can lead to a wide range of adhesive properties.

The selection of PDI for PSA applications depends on the specific application requirements. A low PDI is generally preferred for applications that require consistent adhesive performance, such as high-performance applications. On the other hand, a higher PDI can be used for applications where a wider range of adhesive properties is acceptable, such as low-

performance applications. In addition, the selection of PDI can also depend on the polymerization process used to produce the PSA. Different polymerization processes can result in different PDIs, and the choice of polymerization process can depend on the specific requirements of the application.

Overall, the molecular weight, particle size, PDI, and PDS of the resulting polymer were targeted based on the specific application requirements of the PSA. Testing and evaluation of the PSA performance were used to identify the most suitable molecular weight, particle size, PDI, and PDS for the application.

Additives

Additives such as crosslinkers and chain transfer agents (CTA) can be added to the acrylic emulsion to tailor the properties of the resulting PSA. The use of a chain transfer agent can have significant effects on the properties of the resulting polymer, including its molecular weight, molecular weight distribution, polymer morphology, and overall properties. The selection of crosslinker and CTA for a specific polymerization process depends on several factors, including the desired properties of the resulting polymer and the type of monomers used in the polymerization process. It is important to carefully consider the concentrations of the two in the polymerization process to ensure that the desired properties of the resulting polymer are achieved.

Polymerization Method & Steps

Emulsion polymerization involved two main steps: pre-emulsion preparation and polymerization. During pre-emulsion preparation, monomers and emulsifiers are added to a water phase with stirring to form a stable emulsion. The resulting pre-emulsion was checked for stability before being fed into a reactor. During polymerization, the pre-emulsion was added to the reactor with water, and part of surfactants. The reactor is heated to the desired temperature, and the pre-emulsion is fed into the reactor at a controlled rate. The reaction is monitored, and the reaction parameters are adjusted as necessary. Once the desired degree of polymerization was reached, the reaction was stopped, and the resulting emulsion polymer was recovered by filtration. Overall, the size and distribution of the polymer particles in the emulsion can be controlled by adjusting the rate of feeding the pre-emulsion into the reactor during polymerization.

Testing

180^0 peel, ½" X ½" X ½ kg shear, and 1" loop tack testing was used as per PSTC test methods, to evaluate the performance of pressure-sensitive adhesives (PSAs). Emulsion PSA was coated on the 0.5 mil PET film using Myer rod, and dried in convection over at 80^0C. All the testing were carried on stainless steel (SS) panels. Peel testing measures the adhesion strength of a PSA by measuring the force required to peel the tape away from the substrate. Shear testing measures the cohesive strength of a PSA by measuring the time required for the tape to fail or slide along the substrate under a constant load. Loop tack testing measures the tackiness of a PSA by measuring the force required to break a loop formed by the PSA tape. The results are

used to evaluate the performance of PSAs and to optimize their formulations for specific application.

Polymer and emulsion analysis was carried out using several techniques such as particle size analysis, molecular weight analysis, differential scanning calorimetry (DSC), and rheological analysis. Particle size and distribution analysis was carried out using dynamic light scattering, laser diffraction. Molecular weight and PDI analysis was done using gel permeation chromatography (GPC). Differential scanning calorimetry (DSC) measures the heat flow associated with thermal transitions, such as the glass transition temperature (Tg) and was used to find Tg of the polymer PSA.

Scale-up

The scale-up of emulsion polymerization PSA was carried out from laboratory-scale (2 lbs) to production scale (15000 lbs) in two distinct steps, first to pilot-scale (100 lbs), and later to larger production scale. At laboratory scale the process variables such as temperature, pH, initiator concentration, surfactant concentration, monomer concentration, agitation rate, and reaction time were optimized to obtain a stable emulsion, narrow particle size distribution, and high monomer conversion.

After optimizing the laboratory-scale process, we transferred the process parameters to a pilot-scale reactor with the increment in linear proportion with relevant engineering conversion. Conducted pilot-scale trials to ensure that the process can be repeated and the optimized process parameters can be maintained and well correlated to a larger scale reactor.

Result and Discussion

In essence, surfactants play an essential role in stabilizing emulsions, and the right combination of surfactants can ensure that the emulsion remains stable during the polymerization process. Anionic surfactants have negatively charged hydrophilic groups that create a stable layer around droplets, while nonionic surfactants reduce interfacial tension between the droplets and water phase. When used in combination, they can provide improved stability and better control over the particle size and distribution of the resulting polymer particles. Additionally, the surfactant package to the fixed monomer composition ratio needs to be adjusted to ensure that the surfactant package is effective in creating a stable emulsion.

In the lab, the final formulation of a polymer was adjusted by adding APE-free, ionic and nonionic surfactants, which were chosen based on their emulsification efficiency. Surfactants form a protective layer around dispersed monomer droplets, stabilizing the emulsion. Anionic surfactants have negatively charged hydrophilic groups that create a stable layer around droplets and provide electrostatic repulsion, while nonionic surfactants reduce interfacial tension between the droplets and water phase. The combination of anionic and nonionic surfactants provides improved stability and better control over the particle size and distribution of the resulting polymer particles.

Due to the paper's primary focus on the scale-up effects of reactive surfactants and the importance of maintaining confidentiality, the specific ratio of surfactant package to monomer composition cannot be disclosed. However, the general concept remains the same that the appropriate balance of surfactants is crucial in efficiently emulsifying the monomer and forming

a stable emulsion. In addition, reactive surfactants may have a different effect on the emulsion stability compared to non-reactive surfactants, and it is important to consider their impact during scale-up.

The final composition in the lab was tested for the required performance properties as listed in the table 1, below along with corresponding molecular weight, particle size and polydispersity index were measured as well, listed in the table 2.

Table 1. Performance properties of the Sample 625-00 from the replicates of lab batches

Name: Sample 625-00	Value	Test method
180^0 peel on stainless steel (lbs/inch)	1.9	PSTC
Loop tack (lbs)	2.5	PSTC
Shear (1/2"X ½" X 1/2 kg) (minutes)	2957	PSTC

Table 2. Physical and analytical properties of Sample 625-00

Name: Sample 625-00	Values	Test method
pH	4.42	pH meter VWR
Solids (wt.%)	57.2	Drying by weight %
Viscosity (cPs)	120	Brookfield RV viscometer (2/100)
Molecular weight (Mw) (Dalton)	229000	GPC
Polymer dispersity index (PDI)	4.57	GPC
Particle size (nm)	460	Dynamic Light Scattering (DLS)
Gel content (%)	62	Gel fraction extraction

Table 3. The process parameters of the lab run batch

Parameter	Unit	Value

Volume	gallon	0.5
RPM	-	200
Rate of Addition of Pre-emulsion	lbs/min	0.012
Time of Addition of Pre-emulsion	min	180
Temperature of Polymerization	°C	88

To begin the scale-up process, a pilot batch of 500 lbs was prepared. The batch percentage composition of the ingredients remained consistent, and the process parameters, such as the feed rate of pre-emulsion and RPM, were scaled up in a linear proportion. The exotherm was carefully managed at a fixed temperature to ensure the process remained under control.

Table 4. Performance properties of the Sample 625-00 from the 1st pilot scale up batch

Name: Sample 625-00	Value	Test method
180^0 peel on stainless steel (lbs/inch)	2.1	PSTC
Loop tack (lbs)	2.6	PSTC
Shear (1/2"X ½" X 1/2 kg) (minutes)	2000	PSTC

Table 5. Physical and analytical properties of Sample 625-00 from the 1st pilot scale up batch

Name: Sample 625-00	Values	Test method
pH	4.64	pH meter VWR
Solids (wt.%)	56.5	Drying by weight %
Viscosity (cPs)	182	Brookfield RV viscometer (2/100)
Molecular weight (Mw) (Dalton)	149000	GPC

Polymer dispersity index (PDI)	4.39	GPC
Particle size (nm)	495	Dynamic Light Scattering (DLS)
Gel content (%)	64	Gel fraction extraction

Table 6. The process parameters of the 1st pilot scale up batch

Parameter	Unit	Value
Volume	gallon	50
RPM	-	60
Rate of Addition of Pre-emulsion	lbs/min	2.1
Time of Addition of Pre-emulsion	min	180
Temperature of Polymerization	°C	

Upon comparing the lab batch to the pilot scale in the above tables, it can be observed that the 180-degree peel increased while shear decreased during the scale-up. Unfortunately, the shear was not within the targeted range as indicated by the lab level synthesis. The higher peel data and low molecular weight (Mw) with high polydispersity index (PDI) pointed towards higher activity levels of the initiator and chain transfer agent during polymerization, while going from lab to pilot scale. This may be attributed to the decreased surface area to volume ratio while increasing the scale up volume of reactors, which may have caused ineffective heat transfer during the polymerization. Another source of variation might have come from the difference in the mixing levels from the agitations in the two reactors.

The incorporation of reactive surfactants into the polymer during polymerization can enhance the performance of the resulting adhesives. By doing so, the adhesive strength, as well as other properties such as wetting and water resistance, may be improved. However, one must exercise caution while using chain transfer agents during the polymerization process as it may lead to a decrease in the molecular weight of the polymer chain, negatively affecting the performance of the adhesive. Furthermore, a reduction in molecular weight may result in smaller polymer particles and broader particle size distribution (PSD) and PDI of the polymer, which can be detrimental to the adhesive's strength and durability. Therefore, it is essential to strike a delicate balance between using reactive surfactants and chain transfer agents in the

polymerization process to optimize adhesive properties and reduce any negative effects on the molecular weight, particle size, and distribution of the polymer.

As a next step towards improving shear and adhesive performance, the chain transfer agent and initiator was reduced in combination such that the net reduction in both was 30% and 40%. The following table 7 presents the physical, analytical, and performance properties of the adhesive during successive reductions of 10% initiator and 20% CTA; 30% CTA alone; 30% CTA and 10% initiator; and 40% CTA alone.

Table 7. Properties of the pilot scale batches

Parameter	Unit	Control lab batch	Control (1st pilot scale up batch)	-20% CTA - 10 % initiator	-30% CTA alone	-30% CTA -10 % initiator	-40% CTA alone
Peel Strength	Lbs/inch	1.9	2.1	1.76	1.97	1.62	1.72
Loop Tack	lbs/inch	2.5	2.6	2.57	2.24	1.98	2.05
Shear	minutes	2957	2000	2214	6348	9787	10000+
pH		4.42	4.64	4.74	4.05	4.4	4.29
Viscosity	cP	120	182	186	140	172	134
Solids Content	%	57.2	56.5	60.75	57.8	60.25	57.2
Molecular Weight (Mw)	kDa	229000	149000	292000	199000	284000	220000
Polydispersity Index (PDI)		4.57	4.39	5.27	3.65	5.38	4.07
Particle Size	μm	460	495	544	523	538	482
Gel Content	%	62	64	59	52	56	9

The table 7 shows that when the levels of initiator and chain transfer are reduced, a significant increase in the shear time of Sample 625 is observed across all the batches. This means that it takes more time for the polymer to break under shear forces, indicating that the polymer chains are longer and have high entanglement along with gel content.

The reason for this observation can be explained by the effect of initiator and chain transfer on the polymerization process. The initiator is responsible for initiating the polymerization reaction, while the chain transfer agent regulates the chain length by terminating the growing chain and initiating a new one. Therefore, a lower level of initiator leads to fewer polymerization reactions, resulting in longer polymer chains. Similarly, a lower level of chain transfer agent reduces the branching effect, resulting in a more controlled polymerization process with lower PDI.

The increase in molecular weight (Mw) of the polymer chains is due to the longer polymer chains resulting from a lower level of initiator. Longer chains are favored because they offer more sites for the reaction to continue, leading to more significant chain growth. The decrease in the polydispersity index (PDI) is due to the reduced branching effect of chain transfer, which results in a more uniform molecular weight distribution with fewer defects.

In conclusion, reducing the levels of initiator and chain transfer can lead to a more controlled and efficient polymerization process with longer and more uniform polymer chains, resulting in higher shear product.

It is important to note that the observations mentioned above regarding the effect of chain transfer agents (CTAs) on the polymerization process were made while using a reactive surfactant as a part of the polymer chain. When a CTA acts, it generates smaller segments of polymer chains with the surfactant embedded in them. This may lead to higher polydispersity index (PDI). Therefore, it is possible that the reduced PDI observed in batches with a lower CTA alone levels is not seen when in batches with reduction of CTA along with initiator. This is because the reactive surfactant may affect the branching effect of the CTA, resulting in a less controlled polymerization process and higher PDI.

In summary, while the reduction of initiator and CTA levels may lead to a more controlled and efficient polymerization process with longer and more uniform polymer chains, it is essential to consider the presence of reactive surfactants in the polymer chain, as this can affect the PDI and the branching effect of the CTA.

Comparison of Lab Scale with Pilot Scale at Adjusted Amount of Initiator and Chain Transfer Agent.

It is shown that the performance properties obtained at pilot scale up with the reduced level of initiator and chain transfer agent is equivalent to that of lab scale at higher level of initiator and chain transfer level. This effect is mainly due to change in the volume to surface area of the reactors, the heat transfer difference and the agitation during the polymerization. The fact that the performance properties obtained at pilot scale with the reduced level of initiator and chain transfer agent is equivalent to that of lab scale at higher levels of initiator and chain transfer level is an important finding. This effect is mainly due to a few factors, including the change in the volume to surface area of the reactors, the difference in heat transfer, and the level of agitation during the polymerization process.

At pilot scale, the volume to surface area ratio is typically much higher than in the lab scale, which means that there is a higher ratio of volume to the surface area of the reactor. This

has an effect on the polymerization process because it changes the rate of heat transfer and mass transfer within the reactor, which can impact the quality and properties of the final product. By reducing the level of initiator and chain transfer agent, the rate of heat generation is reduced, which allows for better heat transfer and temperature control in the reactor.

Additionally, the level of agitation in the pilot scale reactor is typically different than in the lab scale reactor, which may allow for better mixing and more efficient heat transfer. This can help to promote a more uniform distribution of monomers and other components in the reactor, which can lead to more consistent polymerization and better performance properties in the final product.

Overall, the finding that the performance properties obtained at pilot scale with the reduced level of initiator and chain transfer agent is equivalent to that of lab scale at higher levels of initiator and chain transfer level is an important one for the development of more efficient and effective polymerization processes. It underscores the importance of carefully controlling the various factors involved in the process, including the volume to surface area ratio, heat transfer, and agitation.

Conclusion

In conclusion, surfactants play an important role in stabilizing emulsions during polymerization, and the appropriate combination of anionic and nonionic surfactants is crucial for improving stability and controlling particle size and distribution. Reactive surfactants can enhance the adhesive properties of the resulting polymer, but caution must be exercised when using chain transfer agents, as they can negatively affect the molecular weight and particle size distribution of the polymer. The reduction of initiator and chain transfer levels can lead to longer and more uniform polymer chains, resulting in higher shear product with fewer defects. However, the presence of reactive surfactants in the polymer chain can affect the PDI and branching effect of the CTA, and this must be considered when reducing CTA levels. The finding that the performance properties obtained at pilot scale with the reduced level of initiator and chain transfer agent is equivalent to that of lab scale at higher levels of initiator and chain transfer level underscores the importance of controlling various factors such as volume to surface area ratio, heat transfer, and agitation for more efficient and effective polymerization processes.

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