

Porosity Control of Suspension PVC Resin by Nano-Buffer Materials

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Summary

One of the important factors for dry blend processes of Suspension Polyvinyl Chloride resin is porosity.

Many parameters have direct and indirect impacts on it.

Direct parameters are operationally controlled and related to the selection of a secondary emulsifier, known as a porisifier.

This parameter is controlled by Reaction Recipe parameters, including agitation intensity, emulsifier ratios, catalyst type, polymerizer temperature, conversion rate, interfacial tension, and PVA degree of polymerization.

On the other hand, the indirect parameters are related to system impurity levels in the reactor. Such impurities are originated from two main sources: namely, Vinyl Chloride monomer, (VCM), and charging water quality.

The application of Nano-Buffer materials in the polymerization phase has revealed the economical improvement of resin porosity.

The results have shown porosity improvements in some applications of around 7%, resulting in operating costs reduction of about 15% in some applications.

Introduction

In suspension process used for the manufacture of Poly Vinyl Chloride resin, PVC, liquid vinyl is Catalyst injected in the reactor.

Its charging is done after having a predisposed homogeneous suspension of VCM. Protective colloids are used to prevent dispersed droplets from coalescence. This will also dispersed in water, as 5-150 micron droplets with a mean size of around 49 microns, utilizing suitably designed agitation system.

Primary suspending agents are charged with or immediately after the limited H₂O charging and under agitation.

Secondary emulsifier, porisifier, which is based on hydrolyzed PVA and Monolaurate Sorbitol, are charged to control agglomeration of the partially polymerized droplets during the polymerization reaction course.

On contact of the secondary suspending agent with VCM and H₂O, it spreads itself on the interface. This parameter is related to reactor design criteria and operating conditions and recipe data.

On the other hand, Impurity levels in the polymerization reactor play an important role on PVC resin physical properties, especially its porosity. As a matter of fact, the internal porosity of single granules in S-PVC dry blending and their distribution play an important role in understanding the morphology of the S-PVC for designed industrial applications.

For industrial applications, a test can be carried out by a porosimeter, which provides a relation between S-PVC and Plasticizer ratio.

Suitable buffer materials shall be added during reactor charging to control their impacts on the polymerization reactions and resin quality, thus attaining prime grade products with high productivity.

PH of the dispersion can help the solution in some parts of the secondary emulsifier made up of hydrolyzed polyvinyl alcohol.

Impacts of design parameters on suspension polymerization

Reactor Parameters

With the increase in autoclave volumes for S-PVC polymerization, and in order to obtain a homogeneous suspension, it is necessary to adjust the agitation rate in the reactor.

This will result in maintaining particle size and porosity of the produced resin.

In order to attain the best quality of S-PVC resin, it has been proven industrially that the percentages of primary and secondary emulsifiers are optimal in medium range of agitator intensity.

Emulsifier Ratios

For diminution of primary and secondary emulsifiers ratios which correspond to an immediate drop in primary emulsifier ratio, and therefore is necessary to compensate for qualitative damage through increase of secondary emulsifier ratio. The diminution of ratio leads to the formation of particles with occluded pores, jellified partially or totally.

From industrial experience, both hydrolyzed cellulose and PVA with hydrolysis value between 73%-78% mole are applied as primary emulsifiers and that the use of secondary emulsifiers leads to acceptable solutions. In this process, the injection of water during polymerization is practical to affect the secondary emulsifier economically.

VCM Reactivity and Inhibition time

High reactivity of VCM and reduction of inhibition time means a number of sub-particles initially superior to the norm.

The surface which must be protected during successive phases of agglomeration will also be superior to the norm and to be the capacity of protection given by the primary emulsifier.

Therefore an increase of primary emulsifier is necessary to control particle size increase.

On the other hand, decrease of reactivity of the polymerization system leads to the formation of less porous particles, which means that we have a slight worsening which can be controlled by increase of the secondary emulsifier.

Reaction Time

When reaction time is reduced, Particle Size Distribution tends towards a large product up to giving residues of 40 mesh. To avoid this, both primary and secondary emulsifiers should be increased.

Also, reducing reaction time means worsening the morphology of the particles and generating fish-eyes. Therefore, the secondary emulsifier should be efficiently applied to get the proper particle internal protection.

Polymerized Temperature

With increased polymerizer temperature, it is known that the particle size distribution tends to fine particles, which requires the primary emulsifier decrease.

On the other hand, secondary emulsifier shows a decreasing value with high polymerizer temperature. This is due to the necessity to keep bulk density of S-PVC to an acceptable level for certain applications.

Conversion

Identified additives are selected based on their suitability for internal porosity improvements, especially the secondary emulsifier. Thus we got S-PVC particles which are able to withstand high levels of conversion.

Interfacial Tension

A correlation could be derived from the interfacial tension of the primary and secondary emulsifiers with respect to S-PVC morphology after polymerization.

Also, there exists a strict correlation between the interfacial tension of primary and secondary emulsifiers with bulk density and internal porosity of the resin.

Impurity Levels and Possible Sources

In S-PVC polymerization processes, there are two possible sources of impurities, namely Vinyl Chloride Monomer production and process water demineralization systems which play an important role on polymerization reactions and produced PVC resin properties.

Impacts of VCM Impurities on PVC Resin Quality

It is known that VCM impurities are either derived from VCM monomer production facilities or recycled monomer from Poly Vinyl Chloride polymerization unit.

The first source is mainly due to insufficient VCM purification system, especially Acetylene, Chloroprene, 1-1 EDC, 1-1-1-TCE & C CL4, whereas the second source is due to the recycled VCM from reactors and VCM recovery systems, such as HCl, Oxygen, Acetylene, Butene-1, Cis- Butene & Methyl Chloride.

<i>Impurities</i>	<i>Fresh Monomer</i>	<i>Recycled Monomer</i>
	<i>PPM</i>	<i>Range, PPM</i>
HCL	0.5	108 - 287
Oxygen	--	5 - 400
Ethylene	1.0	1.2 - 15
Propylene	0.5	0.5 - 3.5
Acetylenics	5.0	5.0 - 14.0
Butene ⁻¹	--	0.7 - 7.6
Cis-Butene	--	0 - 0.9
Trans-Butene	--	0 - 1.0
Methyl Chloride	40.0	1550 - 5000
1-3 Butadiene	--	0 - 1.6

Table 1: Depicts the typical range of impurity levels for both the fresh and recovered VCM monomer.

As a matter of fact, VCM impurity levels have the following are the major negative impacts on the PVC resin quality and equipment:

- Poor yellowness index of PVC resin.
- Unpredictable resin particle size and porosity control.
- Reduced resin stability.

- Equipment accelerated corrosion and scale-type build-ups.

From successive charge data of feed stocks with different impurity levels, it has been shown that:

Fig.1 reveals the impact of the butene⁻¹ level increase on resin specifications.

The interpretation of this relation shows the following with respect to butene⁻¹ level increase as follows:

- Increase of porosity.
- Decrease of Average Particle Size.
- Increase of % passing through the 140 mesh screen.

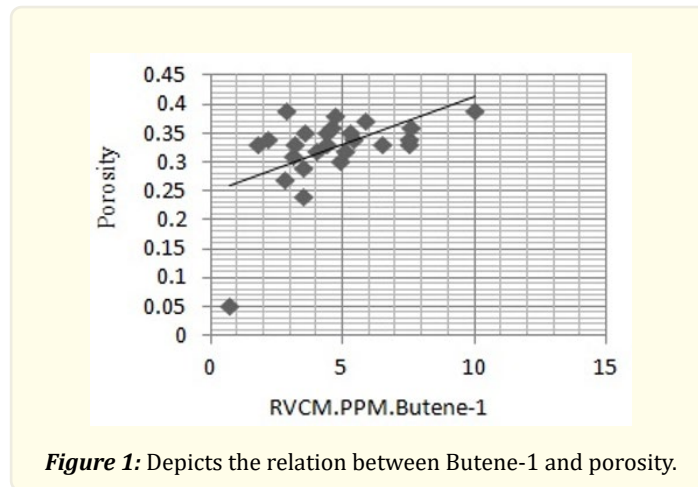


Fig.2 shows the impacts of Oxygen level increase on resin quality as follows:

- Increased porosity.
- Decrease of Average Particle Size.
- Decrease the Average Particle Distribution.

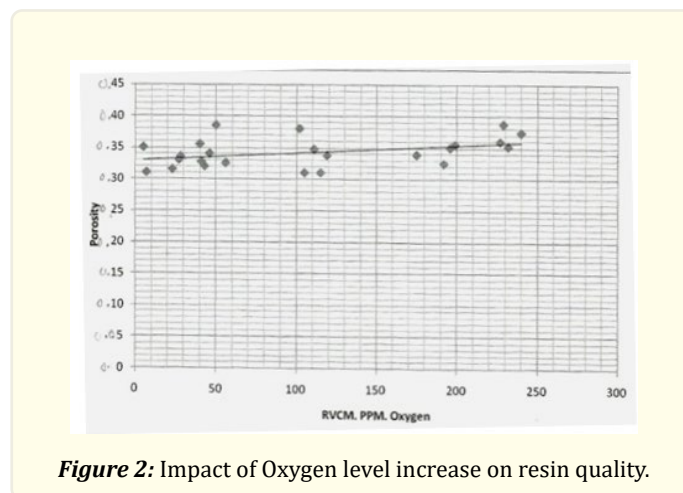
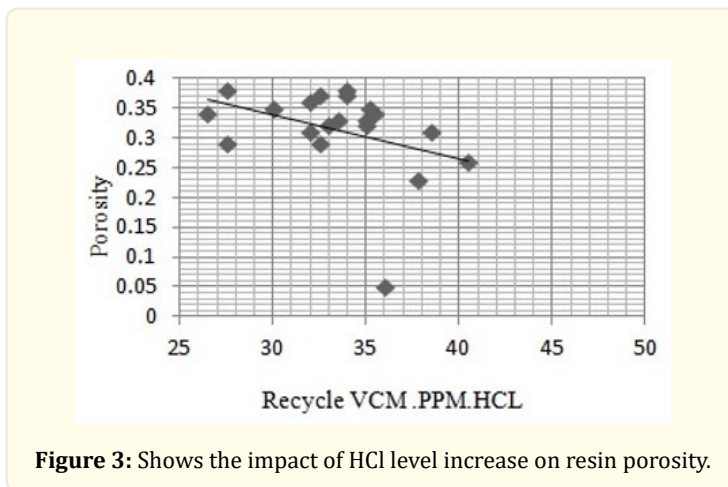


Fig.3 depicts the relation between HCl level increase and resin quality as follows:

- Decrease porosity.
- Decrease Average Particle Size.
- Increase the % passing through the 140mesh screen.



Impacts of Charge Water Specifications on PVC Resin Quality

In suspension polymerization, water has several roles in the process.

It enables the heat distribution of polymerizer contents and help in reducing the slurry viscosity.

Also, it has an important role in carrying the water soluble protective colloids which largely determine the PVC resin morphology.

Therefore, water purity is considered an important feature in suspension polymerization. As a matter of fact, The purity of charge water is affected by the presence of ionic salts such as Fe⁺⁺, SO⁻⁴, Na⁺, CL, SiO₂ total hardness, PH,

ION OR	Resin Type	
	Low temp. resins	High temp. resins
Fe ⁺⁺	1. Methocel in this recipe is very sensitive to Fe. 2. Reduce interfacial activity of PVA. 3. APS-not reproducible.	1. Reduces the interfacial active of polivic. 2. APS very inconsistent.
Total Hard-ness	1. Particle Size increases dramatically as water hardness increases. 2. Cause scale in system.	1. Particle Size increases dramatically as water hardness increases. 2. Also Cause scale in system.
SO ⁼⁴	Reduces the cloud point temp. of Alcotex 72.5 and Methocel F50, also deactivates surfactants.	Affects the cloud point temp. and also deacticates Alcotex 72.5.
Na ⁺	Electrolytes like sodium reduce the cloud point temp. of surfactants and thus reduce their effect as surface active agents.	Sodium at level of 25 ppm cause coarse charges.
pH	pH effect is tied with the level of ions in water: the closer to neutral the better.	Low and High pH levels enhance the frequency of coarse changes.

Table 2: Clarifies the ionic salt’s impacts on S-PVC resin.

Nano-Buffer Material Application

From plant operating data, there has been verified a direct relation between traditional buffer solution level and resin average particle size and its porosity.

The increase of traditional buffer material levels, while keeping other recipe inputs, had an inverse proportionality with porosity and apparent bulk density of the produced resins, which in turn reduce production loads in some compounding applications.

In the S-PVC process units, operational trials have been conducted by nano-scale buffer material, Calcium salts of phosphoric acid, with the formula of $\text{Ca}_3(\text{PO}_4)_2$.

The results have shown porosity improvements in some applications of around 7% without additional secondary emulsifier, while keeping the particle size and PSD in the specified limits.

In other words, the original recipe has been kept without modifying the ratio of primary and secondary emulsifiers, while keeping better reaction stability.

Figs. 4 & 5 show a relation between applied nano-buffer material levels and the resultant porosities for both K 67 & K 70 resins without changing emulsifier ratios of the applied recipe.

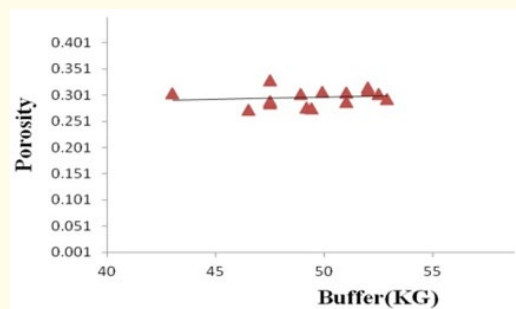


Figure 4: Relation between buffer and porosity for K-67.

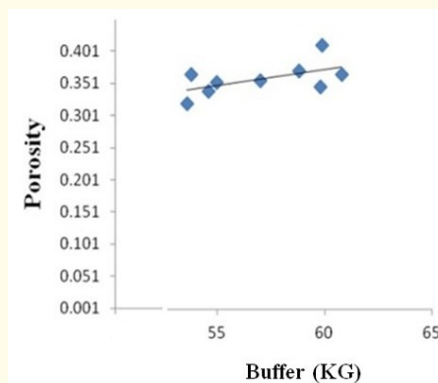


Figure 5: Relation between buffer and porosity for K-70.

From these figures, it can be visualized that there is a direct proportionality between TCP level increase and porosity and average particle size. This can be interpreted to the fact that an increase of TCP will cause a decrease of PVA level in the reactor which in its turn will lead to the increase of resin porosity and decrease its density. On the other hand, the increase of the nano material TCP has led to the increase of APS due to the decrease of PVA, which compensates the impact of PVA reduction in the reactor.

The resulting data can provide an economical tool to control APS level, while maintain a constant porosity, by the application of Nano-TCP material in the polymerization process.

The analysis of these data reveals the enhanced product porosity of the applied modified buffer materials, while keeping prime grade specifications.

Conclusion

Property is an important parameter in S-PVC Compounding, since it affects the speed of plasticizer acceptance.

The application of Nano- buffer materials revealed the enhancement of resin porosity, while keeping the other resin specifications without deviations.

The results have shown improved porosity improvements in some applications of around 7% without additional secondary emulsifier and that other properties have been kept, while keeping particle size and PSD in the specified limits. In other words, resin porosity has been enhanced economically without modifying the ratio of primary and secondary emulsifiers. The resulting operating costs can be reduced by around 15%.

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