Is the Polymer Nature of RDP Driving the Difference in the Performance of a Cementitious System?

**ABSTRACT**

We have designed a multigenerational plan in order to meet the growing performance expectations for redispersible polymer powders in various dry mix mortar applications, allowing product differentiation.

A fundamental understanding of the role of each polymer component is the key to design tailor-made RDP. Manufacturing process of RDP but also microstructure of cement mortar needs to be explored. Polymer latex structure and chemistry, colloidal stabilizer and any extra modifier will impact the final application performance.

The interactions between the polymer and the different colloidal stabilizers have a major effect on redispersibility. Particle size of the latex and choice of monomers will be critical to design the right polymer powder. Those parameters might be necessary to get a redispersible powder but not sufficient to ensure the desired performance in the different construction applications.

A deep look into latex chemistry and colloidal science are taken to approach the major challenges of making a powder that is redispersible and at the same time stable in a cementitious system.

The aim of the present paper is to describe the development process carried out to design the different RDP and the impact in the performance in some of the main dry mix applications.

**INTRODUCTION**

A redispersible powder is by definition a polymer in a powdered form that can be redispersed by adding water to it. The resulting emulsion will fulfill the functionality of a polymeric dispersion binder, normally within a cementitious or gypsum based system. Redispersible powders are obtained by spray drying an emulsion.

Over 90 % of all industrial manufactured polymer dispersions are produced by emulsion polymerization.

By controlling the polymerization process parameters one can control the composition of the final latex, not only in
terms of polymer structure but also in terms of water soluble components that contribute to stabilize the emulsion under extreme conditions; high temperatures during spray dry process and very high pH while used in cementitious systems.

The most important monomers which are being used for applications in the building and construction industry are vinyl acetate, ethylene, versatic acid esters, vinyl chloride, styrene, butadiene, acrylics. The monomers chemistry combination will determine the characteristic of the final film properties like hydrophobicity, saponification resistance, UV resistance, flexibility, adhesion to different substrates etc. but those characteristics well known in a continuous film of a given latex, could not be found when polymer is used in a dry mix mortar at much lower dosage. In a mortar one can only find films domains homogenously distributed along the mortar matrix but not a continuous film. In those cases, polymer chemistry is not directly driving the final performance but other parameter like particle size, stability package etc. that will directly impact powder redispersibility or cement stability.

During the drying step, a protective colloid is added to the emulsion before the spraying. The colloid protects the polymer particles from film forming during the drying process and is also responsible for having the powder redisperse in water again. Over the years polyvinylalcohols (PVOH) proofed to be the most preferred protective colloid for that purpose. In a cementitious system PVOH will be partially saponified and also absorbed on fine particles with in a mortar[2], like cement and fillers. This results in a film forming of the dispersed polymer in a fully coalesced form.

Although PVOH is still the preferred colloidal stabilizer, in the present paper we will show that depending on the polymer chemistry some alternatives to PVOH could be used as long as we have the right steric stability to get the right resistance to high temperature.

The aim of this study is to identify the limits in terms of particle size of primary latex, type and amount of internal and/or external stabilizers to predict redispersibility of a given powder latex and stability of such a powder in a cementitious system to be able to design a RDP with optimized performance depending on the performance application needs.

### METHODS AND MATERIALS

#### Redispersibility

Polymer dispersions in water are spray dried to form a free flowing powder which can be added as polymeric binder in dry-mix mortar formulations. Their performance level depends on their ability to completely redisperse in water and form a film upon drying in the cementitious matrix.

Redispersibility can be measured in various ways.

#### Sedimentation of particles of the diluted redispersion

Large and not redispersed particles will sediment in a pure aqueous dispersion. The less sediment the better the redispersibility will be. This method is usually favored in the daily routine as it delivers well reproducible results.

- 1:1 mixture of water and powder was stirred intensively for 30 min.
- 5g of the final redispersion was mixed with 45g water and filled into a graduated glass tube – diameter of the tube is 1 cm.
- The sedimentation after 1h and 24h (mm) is measured.

#### Particle size distribution of the redispersion

Disaggregation of powder particles in water is measured by laser diffraction. The lower the particle size of not redispersed polymer particles, the better the redispersion will be.

#### Cement Stability

Two different methods were used to characterize cement stability of polymer particle in cement applications.

#### Consistency

Brookfield Viscosity of polymer containing cement/water slurry

- Basic concept of this method is the well known effect of instable polymer particles to agglomerate. Agglomerated particles cause higher viscosity of cement/water/polymer slurry.
- The assumption is that the lower the viscosity, the better the stability of polymer particles will be.
- Cement (CEM I 42.5)/polymer/water ratio (95/5/37 pbw) is constant in all tests carried out during the study.
Sedimentation
– Basic concept of this method is that instable polymer particle cause agglomeration, this agglomeration causes bigger polymer particles, the agglomerated polymer particles show an increased tendency to sediment. Therefore the sedimentation process can be used to characterize the stability of a given polymer dispersion in an aqueous cement slurry.
– Sedimentation of polymer particles can be controlled by different methods. Measuring the turbidity of the water phase or measuring the amount of sediment on the cement phase. In the current study the values are obtained by measuring the light transmission of the water phase on a cement/polymer water (10% mortar/90% water) after a given time.

Cement Based Tile Adhesives (CBTA) according EN 1346 and 1348
Table below shows the dry mix formulation used to run CBTA programs.

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>OPC CEM I 42.5R</td>
<td>35,00 %</td>
</tr>
<tr>
<td>Quartz sand F32</td>
<td>30,60 %</td>
</tr>
<tr>
<td>Quartz sand F36</td>
<td>29,00 %</td>
</tr>
<tr>
<td>RDP</td>
<td>2,50 %</td>
</tr>
<tr>
<td>Modified Cellulose ether (HEMC)</td>
<td>0,40 %</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>100,00 %</strong></td>
</tr>
</tbody>
</table>

Table 1: Cement Based Tile Adhesive Formulation

Four different experimental RDP samples were investigated.

<table>
<thead>
<tr>
<th>RDP</th>
<th>Particle size nm</th>
<th>Tg [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>RDP VAE</td>
<td>960</td>
<td>+17</td>
</tr>
<tr>
<td>RDP Acrylic</td>
<td>860</td>
<td>+12</td>
</tr>
<tr>
<td>RDP Acrylic</td>
<td>170</td>
<td>+10</td>
</tr>
<tr>
<td>RDP SB</td>
<td>250</td>
<td>+8</td>
</tr>
<tr>
<td>RDP SB</td>
<td>150</td>
<td>+8</td>
</tr>
</tbody>
</table>

Table 2: Experimental RDP Samples

 RESULTS AND DISCUSSION

As mentioned in the title of this paper, we would like to answer the fundamental question related to the performance of the different polymer powders when the polymer is a mortar modifier in the sense that is not added as the major binder.

The glass transition temperature of the polymer powder is out of the scope of the present study; we believe that Tg is relevant for given applications like flexible waterproofing membranes where a high (>20%) RDP dosage is required, or to reach the right impact resistance with very low RDP dosage in a base coat adhesive for ETICS. In the present study the application chosen to test our experimental RDP’s is CBTA.

Another statement we need to make before starting the discussion is that “a good powder redispersibility is a necessary condition to get good performance but it is not sufficient”. In other words, a good latex stability at high temperature is required to get a good redispersible powder but if this powder redisperses in water is not stable under high pH conditions or in the presence of a highly ionic environment (cementitious system), the required performance won’t be reached.

All the experimental powders tested in the present study are fully redispersible, so no results related to temperature stability will be presented.
To illustrate the concept of cement stability (figure 1) we have determined the particle size distribution of the water phase of the slurry containing cement, sand, RDP and water (as described in the Methods and Materials section).

The cement slurry is prepared and let sediment for one hour before the particle size distribution is measured. The experimental RDP in the beaker (figure 1) shows a much clearer water phase, proving that the latex is not completely dispersed but sedimented (white layer on the cement bed) and the PSD (grey line) shows larger particles which corresponds to the agglomerates.

The addition of a superplastizicer (SP G1, melamine sulfonate type) enhances the redispersed latex stability as the water phase is whiter showing a higher amount of latex in the emulsion phase and the PSD (green line) shifts to the left hand side, showing the presence of lower particle size latex in emulsion.

This experiment could be translated into consistency values, as shown in figure 2.

In the example presented in figure 2 we could observe the positive influence of superplasticizer enhancing the cement stability resulting in lower consistency paste and on the opposite, the presence of calcium formiate being unfavorable to the cement stability, probably due to the high concentration of calcium ions capturing the PVOH and preventing PVOH to play the role of colloidal stabilizer in a cementitious system.

The combination of consistency and light transmission is well represented in figure 3 where it is shown that consistency and light transmission (as seen in picture of figure 1) perfectly correlate. Higher consistency and higher light transmission (clear water) are caused by more coagulated latex particles and therefore worse cement stability.

In the example of figure 3, experimental RDP prepared using latex of different chemistries are shown.
While comparing stability performance of polymer powders with different chemistries is difficult to conclude, what is the role that polymer chemistry is playing in the cement stability? For the sake of cement stability it seems that the particle size is more critical even though depending on the chemistry a larger particle is necessary. For instance, SB polymer (150 nm) with relatively similar particle to an acrylic base polymer (170 nm) is more stable in a cementitious system.

To validate the relevance of the above information on final application performance we have carried out CBTA tests comparing 5 different polymer powders. The adhesion performance results are summarized in figure 4.

There is a significant difference on overall performance depending on the particle size. Latex particles below 200 nm seem to prevent good adhesion. But there is indeed an impact on the chemistry if we look at the adhesion values after water immersion. The SB powder gives the best, and VAE powder the worst adhesion properties. But if we look at the adhesion after extended open time the preference in chemistry is still different and probably more depending on the overall stability of the system. A very large particle size seems to be the right choice to improve this property. To validate that finding we have designed the experiment as described below:

If we keep our focus on the influence of particle size on the cement stability in a given chemistry, we could really establish the minimum particle size required if we kept the internal/external stabilization system unmodified.

Looking at figure 5, and taking SB as polymer example, a particle smaller than 150 nm could be critical for the sake of cement stability.
At a first glance, one could see a clear trend in terms of cement stability. The smaller particle cause worse cement stability, but actually looking at the sedimentation values, the smaller particle latex gives also a worse redispersibility which also results in higher consistency. But comparing samples of 160 nm and 190 nm that present similar redispersibility values, we see also the same trend. Therefore we could conclude that the smaller the latex particle, the more critical will be the temperature stability hence powder dispersibility and cement stability. As a consequence there will be a lower probability to form a film and contribute to the improved performance in a dry mix mortar.

Internal stabilization could be ionic or non ionic; in general non ionic internal stabilization contribute to enlarge the particle size resulting as shown above in better stabilization. In case internal stabilization is ionic like carboxylic acid, the impact on cement stabilization, contrary to what we initially expected, is also positive as shown in figure 7.

At a given particle size, the larger the amount of carboxylic acid on the latex particle surface, the higher the cement stability of this latex will be.

The results shown in figure 6 on the application tests indicate that the larger the particle of the latex, the better the wettability and the better the open time performance in CBTA will be. Latex with a particle size of 90 nm shows after 20 min only a coverage of approximately 50 % whereas the samples with particle size greater 150 nm have still a coverage of tiles >70 %.

We have analyzed so far the influence of the particle size on the cement stability and furthermore on the application performance, but in the next section we will present the combination of the right particle size with the right amount and type of internal and/or external stabilizer and the impact depending on the nature of those stabilizer (ionic or non ionic).

When stabilizer is external, post added, the effect on cement stability depends very much on the nature of the stabilizer. As shown in figure 8 if the stabilizer is non-ionic it will improve cement stability as its dosage is increased.
However, if the stabilizer is anionic, the effect is just the contrary accelerating the latex collapse, as the light transmission and consistency increase indicates.

Another parameter in favor of using non ionic surfactants to stabilize powder latex in a cementitious system is its relatively low impact on the wet mortar density:

In the table below is shown how the addition of 6 % of anionic surfactant decreases dramatically the density of the wet mortar because it has a much stronger air entrapping effect compared to non ionic surfactants.

<table>
<thead>
<tr>
<th>Type of surfactant</th>
<th>Amount</th>
<th>Wet mortar density g/cc</th>
</tr>
</thead>
<tbody>
<tr>
<td>0%</td>
<td>1.65</td>
<td></td>
</tr>
<tr>
<td>Anionic</td>
<td>6%</td>
<td>1.18</td>
</tr>
<tr>
<td>Non Ionic</td>
<td>3%</td>
<td>1.64</td>
</tr>
<tr>
<td></td>
<td>6%</td>
<td>1.66</td>
</tr>
<tr>
<td></td>
<td>9%</td>
<td>1.65</td>
</tr>
</tbody>
</table>

Table 4: Effect of Powder Stabilizer on Mortar Density

We have proven how critical the primary particle size of the latex is on the overall stability of the system. We have also proven the impact of internal and external stabilizer on the polymer powder performance. The next part of the discussion presents what happens if we combine both particle size and stabilizers to enhance polymer powder wettability performance in CBTA.

As mentioned in the introduction, to make a latex powder redispersible, the addition of a colloidal stabilizer is needed. In general the role it is playing is two folds: to prevent the film forming of the dry powder at temperatures higher than the MFFT of the polymer, but also to enhance the overall stability system for the latex particle in the wet mortar. It is this second role in combination with the primary particle size of the latex that we try to correlate with the wettability of the CBTA mortar.

Figure 9 shows the impact of the amount of PVOH combined with primary particle size on the wettability performance of CBTA.

As expected, the combination of particle size and the amount of PVOH results in a clear improvement of the wettability of the mortar after extended open times. Combining large particle size and high dosage of PVOH shows the best results.

Combining further the learnings on external stabilizers with the aim of minimizing the amount of protective colloid (positive for wetting after extended open time but negative when RDP should be applied at high dosage), we have taken the powders prepared with 7.5 % of PVOH and studied the influence of an external surfactant. This surfactant could also play the role of a protective colloid at lower dosages. It will be called ACS (Alternative Colloidal Stabilizer) in the following section.

Figure 10 shows again that at any primary particle size of the latex the addition of ACS is beneficial for the mortar wettability obtaining the maximum results by combining the larger particle size with the maximum amount (3 parts) of ACS.
CONCLUSIONS

A simple methodology (cement stability test combining slurry consistency and light transmission plus wettability) could be used to quickly predict the final performance of polymer powders in cementitious system.

In general the larger the primary particle size of the latex, the more stable the latex will be in a cementitious system. But the minimum particle size may vary from one polymer chemistry to another.

Although in general anionic stabilizer combined with polymer powders are detrimental for the stability of a cementitious system, in some cases carboxylation as internal stabilizer enhances cement stability and application performance.

The combination of polymer structure with the right stabilization system is absolutely critical to reach the desired performance, however some properties like adhesion after water immersion in CBTA strongly depends on the polymer powder chemistry.

As stabilization plays a key role on the overall polymer powder performance in a dry mix formulation, the right combination and dosage of polymer powder and cellulose ethers will be critical to drive the desired application performance.

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REFERENCES


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