

## Rheology as a tool to fine tune the characteristics of polymer vinyl-acetate / vinyl-versatate dispersions and their behavior in cement mixes

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### ABSTRACT

Vinyl-acetate/vinyl-versatate copolymers in dispersion are widely used as a general purpose bonding aids admixtures for building chemicals. These copolymers are usually stabilized by polyvinyl alcohol working as a protective colloid. Polyvinyl alcohol is usually already present in the polymerization phase, but it can be also post added to further increase the stability of the dispersion. Rheology can be used as a tool to investigate the stability characteristics of this system and further on to study its behavior when mixed with cement for building industry applications.

### INTRODUCTION

Vinyl acetate (VA) vinylversatate (Veova) copolymer emulsions<sup>1</sup> are widely used for interior and exterior building material. Polymer emulsion based on vinyl acetate monomer (VAM) was widely used in the past, but the presence of a comonomer in the chain allows to improve its performances when used in building materials, in the presence of cement. Veova-9 or Veova-10 is often used as comonomer. Polymer use in Portland cement based composites has been known for many years; several publications have shown the benefit of the polymer addition in the properties of the materials like strength, deformability, adhesion, waterproof and

durability for coating. Polymers can also be added in the building chemical formulation in powder form, as redispersible powder.

In this work Va-VeoVa copolymer dispersions have been investigated with rheological tests, and microscopical analysis. In polymer modified products, cement hydration proceeds along polymer film formation. The polymer film is built by coalescence phenomenon that produces an uniform matrix phase with a network structure in which the cement hydrate phase and polymer phase interpenetrate. Many theories have been attempted explain this process, but two are the most reliable to explain how polymers in mortars acts. According to the first theory there are no interaction between the polymer and concrete. During hydration, the hydrophilic part of the polymer is oriented towards the water phase whereas the hydrophobic points toward the air phase (holes, water-free pores). Upon drying, the water leaves, and hydrophobic particles coalesce and form the film. The second theory based on some chemical reactions occurring between the particle surfaces of reactive polymers and calcium ions ( $\text{Ca}^{2+}$ ), that creates a reinforcement in the cement and produces semi permeable membranes.

## EXPERIMENTAL

### Materials

The dispersion of vinyl-acetate/vinyl versatate used in this work was produced by Vinavil R&D Laboratory; in Table 1 Va-VeoVa copolymers dispersion physical characteristics are shown.

Table 1. Polymer physical analyses.

|                                       |      |
|---------------------------------------|------|
| Solid content                         | 50.7 |
| Apparent density [g/cm <sup>3</sup> ] | 1.07 |
| Particle size [micron]                | 1.67 |
| pH                                    | 5.1  |
| Tg [°C]                               | 25.4 |

Table 2: Cement characteristic.

| Mineralogy.                                      | %      |
|--|--------|
| C3S  | 59.4   |
| C2S  | 17.7   |
| C3A  | 7,3    |
| C4AF   | 4.7    |
| Gypsum CaSO <sub>4</sub> *2H <sub>2</sub> O      | 1.1    |
| Bassanite CaSO <sub>4</sub> *0.5H <sub>2</sub> O | 1.8    |
| Anhydrite CaSO <sub>4</sub>                      | 1.0    |
| Periclase MgO                                    | 1.7    |
| Portlandite Ca(OH) <sub>2</sub>                  | 1.1    |
| Arcanite K <sub>2</sub> SO <sub>4</sub>          | 1.9    |
| Calcite CaCO <sub>3</sub>                        | 3.9    |
| Chemical analysis                                | %      |
| Na <sub>2</sub> O                                | 0.5    |
| MgO  | 3.0    |
| Al <sub>2</sub> O <sub>3</sub>                   | 4.7    |
| SiO <sub>2</sub>                                 | 21.1   |
| P <sub>2</sub> O <sub>5</sub>                    | 0.2    |
| SO <sub>3</sub>                                  | 3.5    |
| K <sub>2</sub> O                                 | 0.8    |
| CaO  | 61.2   |
| TiO <sub>2</sub>                                 | 0.2    |
| MnO  | 0.1    |
| Fe <sub>2</sub> O <sub>3</sub>                   | 2.1    |
| SrO  | 0.1    |
| Physical properties                              |        |
| passing 40 µm                                    | 96.5 % |

The cement pastes was prepared mixing water, Portland cement (CEM 52,5 from Cementi Rossi, Italy see Table 2) and latex. The latex characterized as such, and diluted by adding 5, 10 and 15% of water. Cement pastes were prepared by mixing latex and cement at water cement ratio of 0.7. Latex was diluted in order to obtain a concentration by weight of polymer of 3, 5 and 10%. The composition of the cement paste is reported in Table 3.

Table 3. Identification of cement pastes.

| Id.     | Polymer [%] |
|---------|-------------|
| Paste 0 | 0           |
| Paste 1 | 3           |
| Paste 2 | 5           |
| Paste 3 | 10          |

### Specimen preparation and test methods

The emulsion was tested after dilution by adding distilled water (see Table 4), to evaluate the “instability limit”. Cement pastes were prepared using a laboratory mixer following these mixing steps: 1 min at 500 rpm, 30 s stand by, 1 min at 500 rpm. The total duration of mixing was 2.5 min to give homogeneous suspension.

Table 4. Identification emulsion after dilution.

| Id.     | Added water [%] |
|---------|-----------------|
| Latex 0 | 0               |
| Latex 1 | 5               |
| Latex 2 | 10              |
| Latex 3 | 15              |

### Apparatus

Rheological measurements were performed using a stress-controlled shear rheometer (ARG2 from TA Instruments) equipped with polyacrilate cone plate Ø 40 mm with angle cone of 0° 58' 42" (Fig.1) for polymer dispersion sample. In this geometry the tested material properties is subjected to a uniform shear rate<sup>2</sup>.



Figure 1. Rheometer.

This condition is usually required in rheological tests in order to measure material properties and to get a simple relationship between the measured torque/rotational velocity and shear stress/shear rate. To evaluate cement paste based system it is used a cross hatched plate with 40 mm diameter and 1000  $\mu\text{m}$  gap.

#### Rheological measurements procedure

Typical range of shear rates operating in sedimentation process of solid particles in a suspending liquid<sup>3</sup> are very low considering the fact that displacement of particles at the top of a sample is usually lower than 1 cm and that the duration of this period is about  $10^4$  s, the settling speed is therefore lower than  $10^{-6}$  m/s and the shear rates are lower than  $10^{-2}$   $\text{s}^{-1}$ . Hence the rheological characterization of flocculated suspensions should be best obtained through dynamic viscosity measurements at low shearing amplitude, as opposed to flow measurements. However flow curve tests were performed in order to check the shear viscosity of the latex samples with a continuous ramp procedure from 0 to 1000  $\text{s}^{-1}$  (Fig.2).

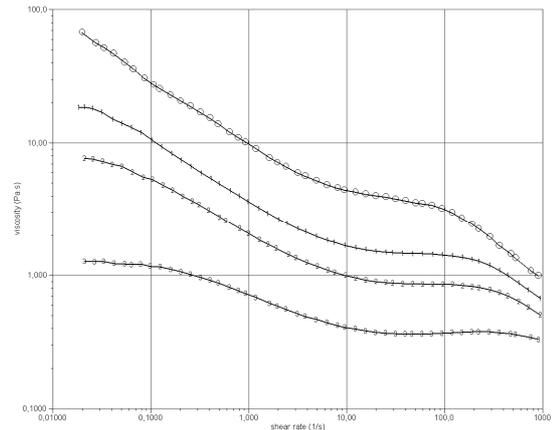


Figure 2. Latex flow curve - O = original dispersion, 1 = Latex 1, 2 = Latex 2, 3 = Latex 3.

Dynamic viscosity measurements were performed by stress and frequency sweep. In the first the stress was increased from 0 to 1000 Pa at constant frequency of 1 Hz; in the second a frequency range from 0.01 to 100 Hz was used at a stress below the critical stress of the system, in the linear viscoelastic region. These experiments allow to determinate the elastic ( $G'$ ) and loss ( $G''$ ) moduli but with different meaning. The stress sweep indicates if the system is prevalently solid or liquid, the frequency sweep gives the relaxation time of the system - or the storage time.

#### Polymer-latex stability characterization

The oscillatory tests is employed for a very fine dispersion, as a Va-VeoVa latex, to evaluate its stability. This test is not destructive and allows to measure the elastic and viscous properties. For a viscoelastic liquid  $G'' > G'$ ; for a viscoelastic solid  $G' > G''$ . In the case of viscoelastic solid elastic behavior dominates and the material will have the tendency to retain its own shape. The nature of dispersion depends on its being prevalently structured or unstructured and the polymerization stabilizer plays a major role.

## RESULTS

### Latex properties

In figure 3 are showed curves of  $G'$  and  $G''$  as a function of shear stress of “Latex” dispersions. Curves show plateau  $G'$  values decreasing as dilution of the reference system increase. Elastic modulus is higher than viscous modulus in system Latex 0, 1 and 2, thereby proving the stability of these dispersions<sup>4</sup>. System “latex 3” has a borderline behaviour: in fact  $G'$  and  $G''$  at low stresses are comparable, and it is sufficient to impose to the sample a stress above  $10^{-2}$  Pa in order to see a prevalence of the viscous behaviour over the elastic one. The 15% dilution can be considered as a limit, above which instability phenomena start.

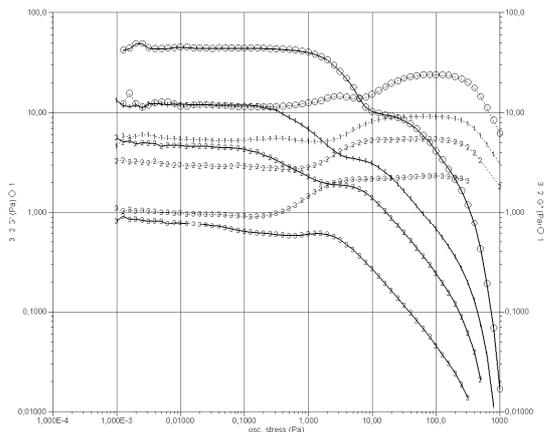


Figure 3. Latex stress sweep - Symbols:  $G'$  = line,  $G''$  = dash line; O = original dispersion, 1 = Latex 1, 2 = Latex 2, 3 = Latex 3.

Frequency sweep test was performed on the same samples, and the results are shown in figure 4. For the same system a modulus increase at high frequencies can be noticed. This behaviour<sup>5</sup> can be explained by time-temperature superposition principle [TTS]: at high frequencies the sample shows the typical low-temperatures behaviour (moduli increase), whereas at low frequencies high temperature behaviour displayed (moduli decrease).

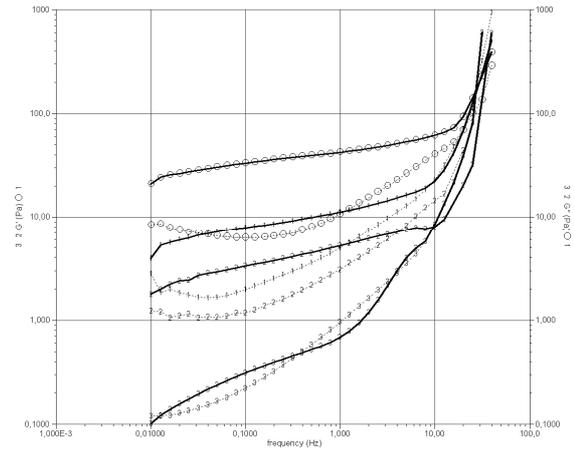


Figure 4. Latex frequency sweep - Symbols:  $G'$  = line,  $G''$  = dash line; O = original dispersion, 1 = Latex 1, 2 = Latex 2, 3 = Latex 3.

In this work frequency sweep test is used to obtain an estimate of the behaviour of the system over time. In practice the test allow to forecast the stability of dispersion during storage, putting in relation low frequency to long time and viceversa. By examining the curves (fig.4) for all system considered as frequency changes, a sharp moduli increase can be notices for frequencies higher than 100 Hz. In the range between 0.1 and 50 Hz, Latex 0, 1 and 2 show a solid behaviour higher than the liquid one, and such characteristics has maintained over time. However as dilution percentage increases, the difference between  $G'$  and  $G''$  decreases, like in the case of Latex 2, showing a liquid characteristics close to solid ones. This is an indication of low stability of the system, further compromised at long storage times.

### Mortar with Va-VeoVa copolymer: rheological behaviour.

Also rheological characteristics of cement pastes have been evaluated with an oscillatory test, and in figure 5  $G'$  and  $G''$  are evaluated as a function of shear stress.

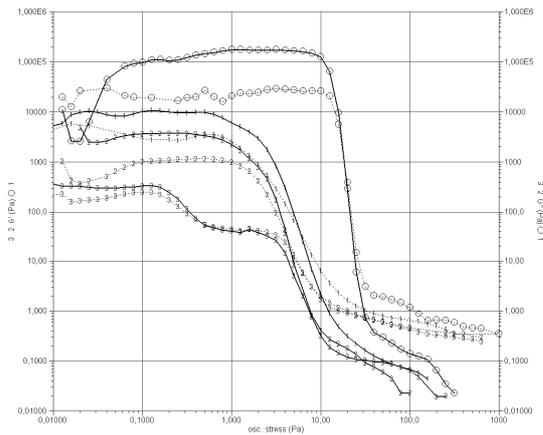


Figure 5. Cement paste stress sweep - Symbols:  
 $G'$  = line,  $G''$  = dash line  $O = 52,51$  w/c: 0.70,  
 1 = Paste 1, 2 = Paste 2, 3 = Paste 3.

The addition of Va- VeoVa copolymer in the cement paste has caused a series of physical effects determined by the coexistence of the two materials. Furthermore measurement is performed right after mixing and the formation of the early hydration products, as reported in literature, are observed about 5 minutes after the cement has been mixed with water. Such effects can be described as follows:

- elastic modulus profile is similar to that reported by literature<sup>6</sup>;
- $G'$  plateau value of pastes, higher than  $10^5$  Pa, describes aggregation in flocs;
- furthermore polymer addition cause cement deflocculation with consequent decrease of plateau  $G'$  and cross over value;
- at Va-VeoVa concentration of 10% elastic modulus  $G'$  shows two yields values.

The hypothesis justifying this behaviour is that at 10% a limit concentration is reached at which the two phases Va-VeoVa/cement system is in equilibrium. This is why the two yields are present, and why the two moduli overlap; as a matter of fact above this concentration the system segregates showing a liquid behaviour dominating over the solid one.

## ESEM investigation

Environmental electron microscope analysis gives the possibility of observing the aggregation state, but not the real dimension of particles, since analytical conditions influence the quantity of water that gets deposited into polymer. The images shown in figure 6, referring to the non-diluted system, show particle population keeping their individuality.

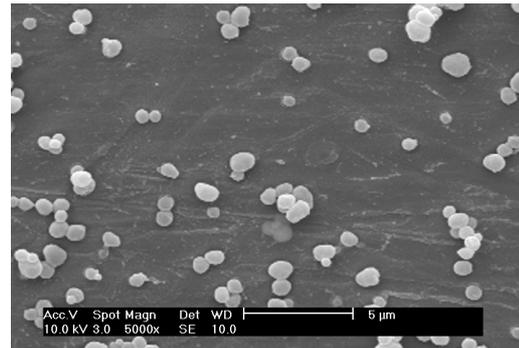


Figure 6. Esem images.

In figure 7 the diluted system is shown, reorganizing in groups as an effect of coalescence, giving birth to flocs the dimensions of which are higher than those of the original particles. This effect is favored by dilution, decreasing the dispersing effect of polyvinyl alcohol, the protecting action of which is decreased by dilution, thereby helping particles fusion.

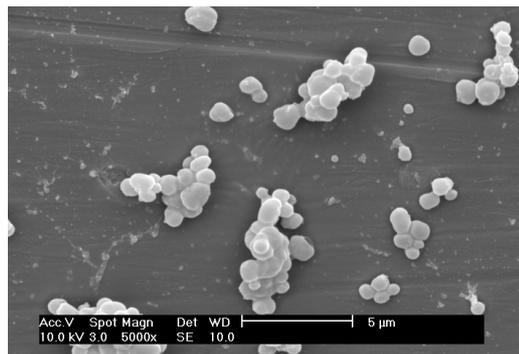


Figure 7. Esem images.

## CONCLUSIONS

The rheology has been shown to be highly sensitive to evaluate the emulsion stability. In this study the analysis of the dynamic modulus of the polymer modified cement paste, allowed a correlation of the fraction of polymer with different parameters, such as the decrease of the storage modulus  $G'$  and the amplitude of the loss modulus  $G''$ . The particular trend of the moduli suggest the arrangement of two different matrices, being one organic and the other one inorganic.

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