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The influence of the PVC ratio of various dispersing agents on the rheological properties of spectrally selective paint coatings for solar thermal application

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ABSTRACT

Rheological tests of TSSS paints for solar absorbers, prepared by using different dispersants (POSS 1, POSS 2 and Dysperbyk180) at various PVC ratios, demonstrated the influence of dispersants on the behaviour of paints during deposition. The optimal PVC ratio was obtained by comparing the rheological results to the spectral selectivity of the final coatings.

INTRODUCTION

Paint coatings for solar absorbers have attracted interest since the introduction of the concept of spectral selectivity[1]. Coatings for which solar absorptance (a_s) depends on the thickness of the applied coatings and the thermal emittance (e_T) of the substrate are called Thickness Sensitive Spectrally Selective (TSSS) coatings. They exhibit excellent spectral selectivity but are thin (~ 100 - 120 nm) and therefore vulnerable to mechanical tearing, can be easily abraded, require careful handling and are not cheap.

In general, paints are organic–inorganic composites consisting of pigment particles evenly distributed (dispersed) in a polymeric (organic) resin binder, additives and solvents[2]. Among the many additives, dispersants are one of the most important. Their use and selection in the course of paint preparation is considered to be the most crucial step in the production of any paint. Dispersants are materials that are capable of providing the compatibility of the pigment particles with the polymeric phase by modifying their surface, which means altering it from hydrophilic to organophilic. The effect of the dispersant can be inferred from the optical properties of the coatings, as well as from the rheological behaviour of the paint during its deposition and the formation of selective coatings. Final formation of the coating is strongly dependent on the rheological properties of the paint[3].

In our work, three different dispersants (commercial Dysperbyk180 and POSS, made in our laboratory) were used at various PVC (pigment to volume) ratios in order to prepare spectrally selective thickness sensitive black coatings for solar absorbers. Various PVC ratios were used in order to determine the best ratio between pigment and binder concentration, which would enable the best technological conditions for the paint application. Moreover, paint with the selected PVC ratio must also assure the best spectral selectivity of the final dry coating.

In order to achieve all the aforementioned requirements, we performed a detailed rheological characterisation of various paints. The paints were deposited on the substrate by the spraying technique at different thicknesses, in order to determine the influence of thickness on the spectral selectivity of the coatings. Measurements of spectral selectivity were therefore performed and SEM micrographs were taken for all final dry coatings.

EXPERIMENTAL

Instrumental

The rheological measurements were performed with a rotational controlled stress rheometer (HAAKE RheoStress 150), equipped with a cone and plate sensor system (C 60/4°).

The spectral selective properties of the paint coatings were determined from the infrared (IR) reflectance spectra. Reflectance in the visible (VIS) and near infrared (NIR) range were measured on a Perkin Elmer Lambda 950 UV/VIS/NIR spectrometer with an integrating sphere (module 150 mm), while the reflectivity spectra in the middle IR spectral range were obtained on a Bruker IFS66/S spectrometer equipped with an integrating sphere (OPTOSOL), using a gold plate as a standard for diffuse reflectance. Solar absorptance (a_s) and thermal emittance (e_T) values were determined from the reflectance spectra using a standard procedure[4].

SEM micrographs were obtained on a FE-SEM Supra 35 VP electron scanning microscope.

Preparation of paint coatings

TSSS paints were prepared using a standard procedure. Black (Mn-Fe spinel black (Ferro, D)) pigment dispersions were first prepared by mixing the corresponding pigment with the lumiflon resin binder in specific proportions and grinding in a ball mill. The concentration (i.e., partial pigment-to-volume concentration ratio, PVC) of the pigment and binder varied from PVC = 22 to PVC = 51.

The paints were deposited on aluminium substrates by a Walther Pilot WA 520 HVLP spray gun with an operating pressure of 2.5 – 3 bar.

POSS 1 and POSS 2 dispersants were made as reported in **[5]**.

RESULTS AND DISCUSSION

Rheological characterization

The influence of dispersants on the behaviour of the paint during deposition was monitored with various rheological tests. Flow curves were performed for all paints prepared and it was observed that all the paints exhibited shear thinning flow behaviour which depended on the PVC ratio. Shear thinning behaviour for dispersant POSS 1 is presented in Fig. 1. It can be seen that the binder (PVC of the paint = 0) exhibited nearly Newtonian flow behaviour, while shear thinning was more pronounced for higher values of PVC ratio. Similar results were observed for all dispersants.

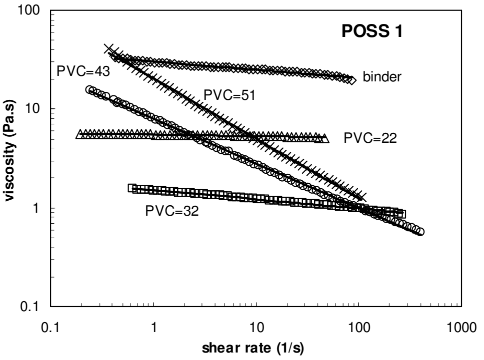


Figure 1: Flow curves of binder and paints with POSS 1 dispersant with different PVC ratios.

The results of flow tests for all the paints were correlated to the Power Law equation (Eq. 1) and, as expected, different values of power law index (n) and consistency index (k) were obtained.

$$\eta = k\dot{\gamma}^{n-1} \qquad \text{(Eq. 1)}$$

In Figure 2, the dependence of the power law index (n) on the PVC ratio is presented. It can be seen that n decreased with increasing PVC ratio for all three dispersants. The decrease of the index n was more pronounced for Dysperbyk180, for which the values of n, compared to POSS 1 and POSS 2, were lowest over the whole range of PVC.

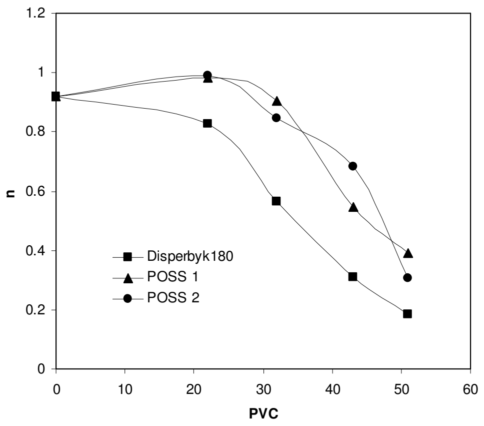


Figure 2: Flow index for paints with different dispersants.

In addition to flow behaviour tests, oscillation tests were performed. Frequency tests, performed in linear viscoelastic range (LVE) are presented in Fig. 3A and B. Fig. 3 presents the influence of the PVC ratio on dynamic modules during the oscillation test for paints with dispersant POSS 2. Over the entire frequency range, both dynamic modules increased with increasing frequency of oscillation.

The influence of the PVC ratio on the rheological behaviour of the paints was observed from the relation between G' and G'' (Fig. 3B). For paints with PVC ratios up to 43, the viscosity module (G'') prevailed over the elastic one (G'); moreover, the prevalence of G'' over G' was more pronounced for lower PVC ratio. For the paint with PVC = 51, the elastic module slightly dominated, moreover both modules were almost independent of the frequency of oscillation. This clearly indicates that PVC = 43 is the highest acceptable value for paints with this dispersant (POSS 2). If the PVC ratio is increased over this value, the concentration of the pigment in the paint is too high, causing the pigment particles to agglomerate. The paint consequently loses its ability to flow, which can cause problems during the application of the paint.

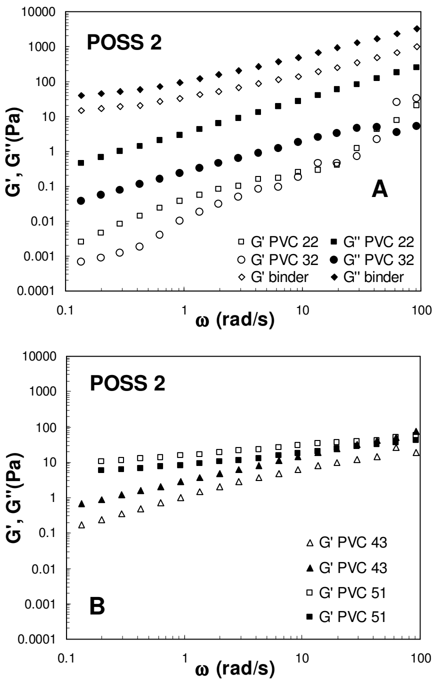


Figure 3: Oscillation tests: frequency dependence of G' and G'' for paints with POSS 2 dispersant. A) Binder and paints with PVC = 22 - 32; B) paints with PVC = 43 - 51.

A similar effect was also observed in paints, made with the other two dispersants (POSS). The difference between dispersants was observed in the corresponding values of the PVC ratio, whereby the dominating effect of the viscous module changes. The highest acceptable PVC ratio for paints with POSS 1 and POSS 2 was 43, while for paints with Dysperbyk180, this value was lower (PVC = 32).

In order to obtain a smooth and homogenous final coating, the paint should exhibit viscoelastic properties that enable a controlled deposition of the paint on the substrate and good recovery of the paint after the application. In order to examine the recovery of the paints prepared by the different dispersants, time tests were performed (Fig. 4) in three steps. In the first step, the conditions at rest were simulated (oscillation in the linear viscoelastic range). The second step simulated the conditions during paint deposition (rotation at high shear) and the third step was the same as the first, in order to simulate the conditions of film formation (recovery after high shear). The same tests were performed for all dispersants, as well as for the binder.

Similar results were observed for all dispersants used, so only the results for paints with Dysperbyk180 are presented in Fig. 4. It can be seen from the figure that, by analogy with the frequency tests, the viscous module (G'') prevailed over the elastic one (G') for paints with PVC lower than 32 (for dispersant Dysperbyk180, shown in Fig. 4). During the constant conditions (constant frequency of oscillation) in the 1st step of the experiment, G' and G'' were constant (especially for lower PVC ratios). This indicates that these paints were stable at rest. Some instability in G' and G'' were observed for higher values of PVC ratios; both modules increased with time at a constant frequency of oscillation. This is in agreement with our observations that higher PVC ratios cause some instability (i.e., agglomeration) in the paints.

After the application of high shear in the 2nd step, the conditions of constant frequency were applied in the 3rd step. It was observed that for all PVC ratios, G' and G'' gradually increased until they reached the initial values, i.e., recovery was complete. Recovery was slowest for the binder and fastest for higher values of PVC ratios. For PVC = 51, recovery was practically instantaneous, which indicates that the levelling of the paint would be too fast to allow the formation of a smooth and homogenous coating.

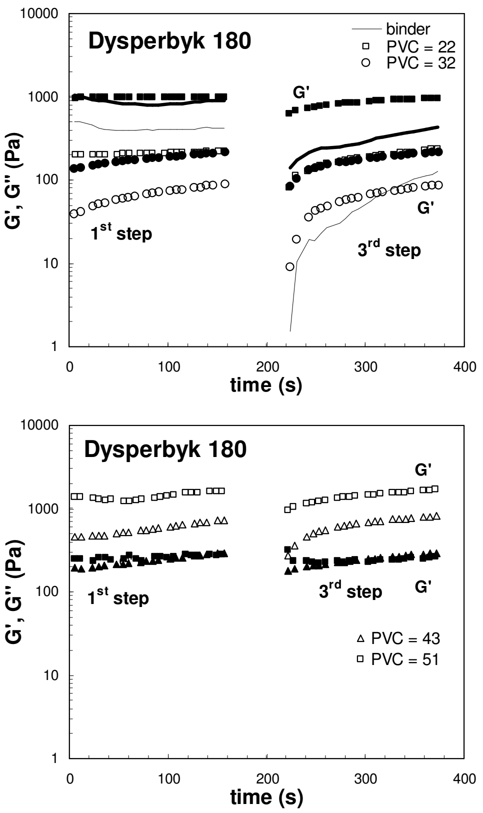
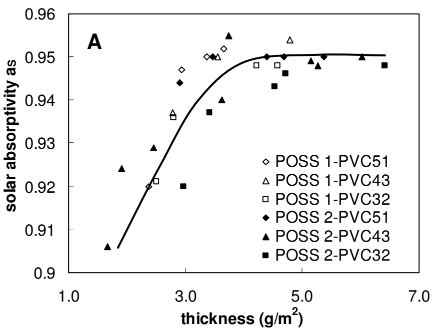


Figure 4: Time tests: the dependence of dynamic modules (G', G'') on time (three steps: 1st - oscillation in LVE, 2nd - high shear, 3rd - oscillation in LVE) for paints with dispersant Dysperbyk180.

Spectral selectivity of TSSS coatings

Various dispersants were examined in order to obtain thickness sensitive spectrally selective (high a_s and low e_T values) final dry coatings for solar absorbers. Since these paints are thickness sensitive, the influence of the thickness of the coatings with different PVC ratios was also examined (Fig. 5). It was observed that emissivity and absorptivity depended mainly on thickness and less on the PVC ratio or the type of dispersant used. Both emissivity and absorptivity increased with increasing thickness (in g/m^2), so the optimal coatings should be thin (also the lowest values of thickness exhibit relatively high values of $a_s > 0.9$).



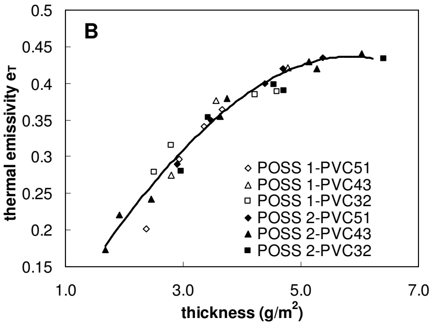


Figure 5: The dependence of spectral selectivity on the thickness of final coatings: A) solar absorptivity; B) thermal emissivity.

Spectral selectivity was also examined for the binder (Fig. 6) and it was observed that the emissivity of the binder linearly increased with increasing thickness.

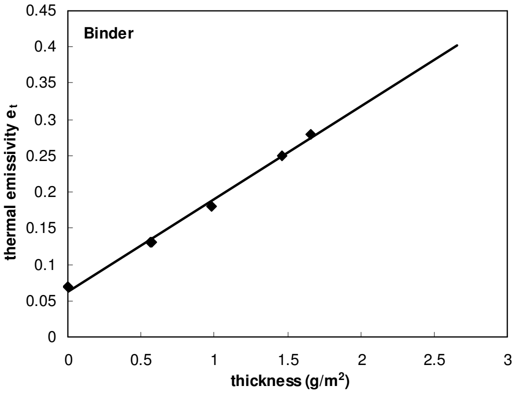


Figure 6: Dependence of thermal emissivity on the thickness of the binder deposited on the substrate.

SEM measurements

SEM micrographs were taken in order to observe the influence of pigment loading, i.e. the PVC ratio on the morphology of the final dry coatings. Fig. 7 shows the differences between low (A) and high (B) values of PVC ratio for dispersant POSS 2. It can be seen that for low values of PVC ratios (Fig. 7A), the coating is sparsely covered with the pigment, while at higher values of PVC (Fig. 7B), the distribution of the pigment is very dense and uniform.

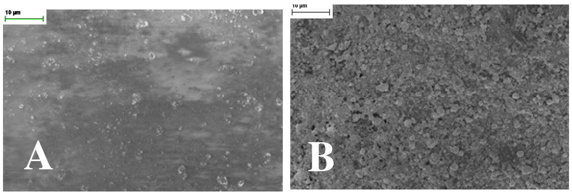


Figure 7: SEM micrographs of coatings with low (A) and high (B) PVC ratio.

CONCLUSIONS

Rheological tests of TSSS paints showed that the influence of different dispersants on the behaviour of the paints during deposition was minimal for PVC ratios below 0.32. For all the paints, the flow behaviour index (n) decreased with increasing PVC ratio down to a value of n ~ 0.15. All the paints exhibited viscoelastic behaviour for all PVC ratios studied. Oscillation tests showed that the liquid-like behaviour of the paint changed to solid-like behaviour at PVC = 32 for Dysperbyk180 and at PVC = 43 for POSS 1 and POSS 2, respectively. Moreover, the optimal ratios between a_s and e_T (high a_s and low e_T values) were obtained for PVC ~ 43, which we are currently use for the preparation of spectrally selective paints.

To conclude, results of rheological tests confirmed that POSS materials can act as superdispersants. These materials are prerequisite for the production of selective paints, because they enable the preparation of dispersions with higher pigment loadings (i.e., PVC ratios) compared to the commercially available dispersant, i.e. Dysperbyk180. They provide strong interfacial bonding between the binder and POSS dispersant molecule.

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