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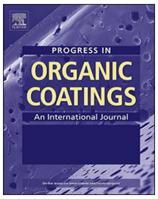

A novel contribution to the modeling of the matting efficiency of aqueous polyurethane dispersions

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ABSTRACT

Gloss is a critical issue in many applications in the coating industry. Gloss depends on optical and rheological properties of complex mixtures, and estimating gloss from basic properties is still a challenge. In order to predict the gloss of an industrial thickened-to-application formulation this work presents a gloss-rheology semi empirical-modeling approach based on a gloss excess function and previous work from other authors. A new matt (low gloss) hybrid waterborne polyurethane dispersion composed out of a self-matting agent (A) and a traditional silica-based matting agent (B) has been studied, and the resulting gloss of the mixture has been correlated to pure component gloss values and dynamic viscosity at medium shear rate. Several modeling options have been tested and their goodness of fit has been determined. The most promising options have been selected and validated towards untrained data sets.

1. Introduction

Serviceable engineering components not only rely on their bulk material properties, but also on the design and characteristics of their surface [1]. The tannery sector, particularly the automotive coatings division, is well aware of this fact. The finish of their products often has to meet opposite needs [2] requiring complex and expensive hands-on formulation procedures. In order to comply with current environmental legislation [3] and to maintain competitiveness [4], most companies rely on the use of waterborne polyurethane dispersions (PUD's). An aqueous PUD is a binary colloid system in which polyurethane particles are stabilized and dispersed in a continuous aqueous medium [5]. Such compounds provide great haptic quality, durability and excellent appearance.

One of the most commonly used parameters in appearance evaluation is gloss [6] since it generally has direct bearing upon the product's serviceability [7]. Gloss can also be related to the overall performance allowing early troubleshooting. According to the NIST gloss can be defined as the function of luminous directional reflectance of a specimen, responsible for its shiny or lustrous appearance. Concerning car-upholstery and inner vehicle decorations, a strong matt (low gloss) finish is currently demanded by customers [8] so as to recall toughness, seriousness, luxury and provide a glare-safe driving experience.

Matting properties are utterly related to surficial light-matter interaction and have no direct correlation with chemical structure [9]. The presence of inorganic particles (e.g SiO_2, TiO_2) and/or other innovative self-matting agents (MA's) in the PUD produce the necessary dry-film roughness for light to be properly scattered. Despite the common belief that self-MA's are to phase out traditional metal oxide MA's, no functional pure self-MA solutions have yet been found. A plausible meantime solution involves the synergic blending of MA's [10,11] as used for other advanced application fields [12]. Those mixtures are known as hybrid MA's and are growing in popularity [13].

Being able to estimate, tailor and economically exploit the matting efficiency of their product portfolio would be of high interest to any MA manufacturer. Nevertheless, there is a lack of full understanding between the coating process parameters and the final quality properties of the coating, as well as a consequent absence of standard, specialized, industry-friendly simulators. Hence, encouraging the development of predictive models is a challenging and necessary task [14].

This study proposes a first modeling approach towards a general simulation and optimization framework for the PUD-based coating division, which will provide better process and product understanding and will help the design and further optimization of their products. Thus, the main aim of this study is to find a tool for predicting the final gloss of a thickened-to-application, hybrid-MA.

2. Modeling approach

The problem under study involves two main steps. The first one

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concerns the actual mixture of both matting agents and its additives. The second one involves the thickening of the matting mixture for application purposes. It may be modeled as follows:

$$\begin{cases} A + B + X \rightarrow m & \textit{Mixing stage} \\ m + T \rightarrow M & \textit{Thickening stage} \end{cases} \tag{1}$$

where $\boldsymbol{A}$, $\boldsymbol{B}$ and $\boldsymbol{X}$ are the initial raw materials and auxiliaries, which yield mixture $\boldsymbol{m}$. With the addition of thickener $\boldsymbol{T}$ the viscosity of $\boldsymbol{m}$ raises and becomes the thickened mixture, $\boldsymbol{M}$. Considering both stages, the total gloss change Δg_{Tot} could be expressed as:

$$\Delta \mathrm{g}_{\mathrm{Tot}} = \Delta \mathrm{g}_{\mathrm{mix}} + \Delta \mathrm{g}_{\mathrm{thick}} \tag{2}$$

Where $\Delta \mathrm{g}_{\mathrm{mix}}$ denotes the gloss change in the mixing stage whilst $\Delta \mathrm{g}_{\mathrm{thick}}$ represents the gloss change with the addition of the thickener. Developing Expression (2), where $\mathrm{g}_{\mathrm{ref}}$ represents a gloss ground state referred to the raw material's gloss:

$$g_M - g_{ref} = g_m - g_{ref} + \Delta g_{thick} \rightarrow g_M = g_m + \Delta g_{thick} \tag{3}$$

Hence, two mathematical models are to be found:

- Mixture's gloss, g_m
- Gloss change due to the thickening, Δg_{thick}

Despite the thermochemical similarities of the modeling approach, gloss cannot be treated as a state function. This is because it is a rheology-related variable and PUDs present viscous hysteresis. Should an “unthickening” process be possible it will surely not bring the PUD to its initial state (path dependent function).

2.1. *Hypothesis*

There are some assumptions upon which the different mathematical models are built:

- The hybrid-matting agent can be satisfactorily described by the gloss of product A (g_A), the gloss of product B (g_B), and the dynamic viscosities of the mixture (μ_m) and of the thickened mixture (μ).
- All dynamic viscosities are referred to medium shear rate conditions ($\dot{\gamma} = 50\ \mathrm{rad\,s^{-1}}$) due to an experimental observation concerning a plateau formation in the rheology curve ($\dot{\gamma}$ vs μ) along with other application-related issues.
- The gloss of the thickened mixture is a fraction of the mixture's gloss.
- Matting agent concentration remains constant during the thickening since only up to 0.34 g of thickener is added.
- There is no effect of the additives (**X**) in gloss or viscosity.
- Mixture's gloss can be determined without taking into account the viscosities of product A and B since $\mu_B \ll \mu_A$ then $\mu_m \approx \mu_A$ and these results where confirmed with some experimental attempts. Though the main scope of this contribution is focused on the rheo-optical model this feature will be addressed in future work due to its evident practical interest.

2.2. *Mixture model*

When polymers or macromolecules are present in a mixture such systems do not generally follow ideal mixing rules. That is that their mixture properties cannot only be predicted only by taking into account contributions like weight, molar or surface fractions. In order to tackle that complexity, the use of an empirical gloss excess function is proposed in this paper taking as a basis a weight-fraction mixing rule. Let g_E be an excess gloss function (EGF) that will account for the deviations between experimental values (g_{exp}) and ideal mixing rule behaviour (g_{ideal}). Consequently:

$$\mathrm{g}_{\mathrm{E}} = \mathrm{g}_{\mathrm{exp}} - \mathrm{g}_{\mathrm{ideal}} \tag{4}$$

According to Eq. (4) a suitable model for representing the experimental mixture data, or g_m, would be:

$$g_{exp} \approx g_m = g_{ideal} + g_E \tag{5}$$

The ideal contribution term could be represented by various mixing rules. Following the thermochemical-like nature of the model a logarithmic mixing rule will be used. This could be related to the fact that matting efficiency is related to randomly scattered light and compared to other polymer-related expression where disorder is relevant. The EGF term will be considered as a function of $\mathrm{g}_{\mathrm{A}}$and/or g_{B} in good agreement with the g_E is by direct inspection of the following plots: $\mathrm{g}_{\mathrm{exp}} - \mathrm{g}_{\mathrm{ideal}}$ vs $\mathrm{g}_{\mathrm{A}}^{*}\mathrm{exp} - \mathrm{g}_{\mathrm{ideal}}$ vs $\mathrm{g}_{\mathrm{B}}^{*}$ where $\mathrm{g}_{\mathrm{j}}^{*}$ is a linearized form of gloss: $\mathrm{g}_{\mathrm{j}}^{*} = g_j, \ln(g_j)\ldots.$

2.3. *Thickening model*

The mathematical model derived in this section intends to represent the transition from the mixing stage to the thickened stage. That is how, when viscosity is raised, gloss actually decreases. This effect is mainly related to the fact that the more viscous the mixture becomes the more entrainment between particles and matting structures occurs and their settling speed is slowed, increasing surficial roughness. In good agreement with this experimental evidence, thus:

$$\Delta g_{Thick} \leq 0 \tag{6}$$

Furthermore, assuming that the gloss of the thickened mixture is a fraction f_T of the gloss found in the unthickened mixture:

$$g_M = g_m - f_T\, g_m = g_m(1 - f_T) \tag{7}$$

Gloss and rheology can be related by means of other meaningful coating-like variables. For instance matting agent concentration c or concentration ratio towards critical matting agent concentration $\theta = \frac{c}{c_{crit}}$ have been used [15]. Taking the following equations as a basis for the model:

$$-\frac{dg}{dc} = g_{eff}\left(\frac{g}{1 - \kappa_g c}\right) \tag{8}$$

$$\frac{d\mu}{dc} = \mu_{eff}\left(\frac{\mu}{1 - \kappa_\mu c}\right) \tag{9}$$

Where g_{eff} and μ_{eff} are κ_g and κ_μ are dispersion quality parameters, depending on matting agent concentration, critical matting agent concentration and film drying rate.

Lacking a more thorough knowledge, κ_j is approximated by the following expression in which, for simplicity, the initial quality dispersion κ_j^0 parameter for both gloss and viscosity takes the same value:

$$\kappa_j = \kappa_j^0 - \left(\kappa_j^0 - \frac{1}{c_{crit}}\right)\theta \ \text{ with } \kappa_j^0 = \kappa^0\ \forall\, j \tag{10}$$

A concentration independent gloss-rheology model is to be obtained. This is reasonable, since the actual change in matting agent concentration due to the addition of the thickener is lower than 1%. Dividing (8) by (9):

$$-\frac{dg}{d\mu} = t\frac{g}{\mu} \text{ where } \mathrm{t} = \frac{g_{eff}}{\mu_{eff}} \tag{11}$$

Integrating (11) between $g_m > g$ and $\mu_m < \mu$ Eq. (12) is obtained:

$$g = \left(\frac{\mu_m}{\mu}\right)^t g_m \tag{12}$$

After rewriting the viscosity ratio $\frac{\mu_m}{\mu}$ as R, the gloss depletion factor f_T can be readily derived:

$$f_T = 1 - R^t \tag{13}$$

Note that this single-parameter model meets the no thickening