

PREDICTION OF ZERO SHEAR VISCOSITY OF POLY (VINYL CHLORIDE) PLASTISOLS

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Received: 12.1.2006, Final version: 9.3.2006

ABSTRACT:

The rheological behaviour of PVC plastisols composed of a blend of suspension and micro-suspension resins in different proportions was investigated. The present work was mainly focused on the variation of the zero shear viscosity versus the concentration of the extender resin. Hence, the packing fraction Φ_m was evaluated using the Krieger-Dougherty equation. These experiments confirmed the major influence of particle size distribution concerning the decrease of viscosity for concentrated suspensions. In addition, a model based on the porosity model developed by Ouchiyama et al. (Ouchiyama N, Tanaka T: Porosity estimation for random packings of spherical particle", *Ind. Eng. Chem. Fundam.* 23 (1984) 490-493) to predict the packing fraction in the case of multimodal lattices was successfully applied to our PVC plastisols formulations.

ZUSAMMENFASSUNG:

Das rheologische Verhalten von PVC-Plastisolen, die aus einem Blend einer Suspension und Mikrosuspensionen mit unterschiedlichen Mischungsverhältnissen bestehen, wurde untersucht. Die gegenwärtige Arbeit zielte hauptsächlich auf die Variation der Schernullviskosität als Funktion der Konzentration des Extenderharzes. Daher wurde die Packungsdichte Φ_m mit Hilfe der Krieger-Dougherty-Gleichung ausgewertet. Diese Experimente bestätigen den dominierenden Einfluss der Partikelgrößenverteilung hinsichtlich der Abnahme der Viskosität bei konzentrierten Suspensionen. Darüber hinaus wurde ein Modell, das auf einem von Ouchiyama et al. entwickelten Porositätsmodell basiert (Ouchiyama N, Tanaka T: Porosity estimation for random packings of spherical particles, *Ind. Eng. Chem. Fundam.* 23 (1984) 490-493), erfolgreich auf unsere PVC-Plastisol-Formulierungen angewandt, um die Packungsdichte für multimodale Gitter vorherzusagen.

RÉSUMÉ:

Le comportement rhéologique de plastisols de PVC composés d'un mélange de suspensions et de micro-suspensions de résines dans différentes proportions a été étudié. Ce travail est principalement centré sur la variation de la viscosité de cisaillement à vitesse nulle en fonction de la concentration en résine. A partir de celle-ci, la fraction volumique pour le compactage Φ_m a été évaluée en utilisant l'équation de Krieger-Dougherty. Ces expériences ont confirmé l'influence majeure de la distribution en taille des particules sur la diminution de la viscosité pour les suspensions concentrées. De plus, un modèle basé sur le modèle de porosité développé par Ouchiyama et al. (Ouchiyama N, Tanaka T: Porosity estimation for random packings of spherical particle", *Ind. Eng. Chem. Fundam.* 23 (1984) 490-493) afin de prédire la fraction volumique de package dans le cas de réseaux multimodes, a été appliqué avec succès à nos formulations de plastisols de PVC.

KEY WORDS: PVC plastisols, rheology, particles size distribution, maximum packing fraction

1 INTRODUCTION

Predicting the evolution of the viscosity of PVC plastisols is extremely difficult. This complex rheological behaviour results from the physics of particles in suspension whose complexity is enhanced by the complexity of PVC plastisols formulations (origin of PVC; mineral fillers; surfactants ...). Particles of PVC are subject to different types of interactions (Van der Waals, brownian, electrostatic) but cannot be considered as solid

particles because interactions with plasticisers lead to their swelling upon heating and consequently, completely modify their apparent volume fraction [1]. Yet, the fluidity of plastisol before its gelification governs its stability and easiness of processing. Therefore, it would be interesting to be able to predict it and as results adjust it if needed.

Rheological studies performed on standard lattices [2 - 23] are a solid source of documents for the more fundamental study of the rheology

© Appl. Rheol. 16 (2006) 136–144

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136

Applied Rheology
Volume 16 · Issue 3

This is an extract of the complete reprint-pdf, available at the Applied Rheology website

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according to the best fit of the Krieger equation, $[\eta]_o$ equals to 4 for the monomodal resin B and $[\eta]_o = 4.6$ for the bimodal resin A. In the same way, measurements on the mixtures lead to an intrinsic viscosity ranging between 3.6 and 4.5. In order to predict $[\eta]_o$ of the mixtures, we assumed that

$$[\eta]_o = [\eta]_{o, \text{resinB}} \cdot [\eta]_{o, \text{resinA}} \cdot \Phi_{\text{resinB}} \quad (7)$$

where $[\eta]_{o, \text{resinB}} = 4$ and $[\eta]_{o, \text{resinA}} = 4.5$. Table 3 summarizes the values of intrinsic viscosity evaluated owing to experimental results and calculated from Eq. 7. These values are very close, consequently we regard our evaluation of intrinsic viscosity as correct.

Finally, figures 10 shows the prediction of the model considering tri-modal population. The values of viscosity are well evaluated for the diluted mixtures $\Phi < 40\%$ where the PSD distribution does not play a dominating role. The predictions are also correct for the concentrated mixtures as long as the value of Φ_g remains lower than its optimal value (around 95 %) given by Pishvaei's model and which corresponds to a minimum of viscosity. However, the re-increase of viscosity is not well modelled: it takes place for too large Φ_g and is carried out in a too abrupt way. The problem comes, as already underlined, from the fact that the tri-modal model predicts a maximum Φ_m for a too high value of Φ_g . The difficulty of the modelling of the packing term due to uncertainty on individual Φ_m is thus not reflected on values of viscosity but on the ratio of extender which leads to the lowest viscosity for a concentration Φ . However the region of lowest viscosity can be predicted precisely enough all the more so as our system is poly-disperse.

CONCLUSIONS

We initially checked that the Krieger-Dougherty equation was applicable to PVC plastisols. From this equation and experimental results, we have then determined the packing parameter of two different PVC resins. The knowledge of the packing parameters and the size distributions of particles, allowed us to use the model of Pishvaei et al [3] to evaluate the packing fraction Φ_m of poly-modal mixtures.

From the knowledge of the packing term, we finally go up with the values of zero shear viscosity and thus confirm that beyond a critical concentration $\Phi > 30\%$ and for a ratio δ ranging between 0.07 and 0.5, there is an optimal fraction in large particles Φ_g between 40 and 70 % for which the viscosity is minimal.

Results are compatible with those of the literature relating to lattices and prove that PVC are particular suspensions which obey nevertheless the general laws of dispersions.

This work also underlines that a relatively broad and polydisperse distribution can be modelled in first approximation by a system made up of N monodisperse systems centred around a well defined size. However, this work highlights the faults of the model of Pishvaei [3] since it requires the knowledge of parameters which are difficult to predict, in particular Φ_m and intrinsic viscosity of the mono-modal populations.

ACKNOWLEDGEMENTS

The authors would like to thank Porcher-Industries for providing raw materials and for authorisation to use the results in this report. Further, the authors are grateful to M. Pierre Alcouffe for providing the SEM images.

REFERENCES

- [1] Larson RG: The structure and rheology of complex fluids, Oxford University Press, New York (1998).
- [2] Guyot A, Chu F, Schneider M, Graillat C, McKenna T: High solid content latexes, Progress in Polymer Science 27 (2002) 1573-1615.
- [3] Pishvaei M, Graillat C, Cassagnau, McKenna T: Prediction the viscosity of bimodal latex based on the method of maximum packing fraction, Chemical Engineering and Science, submitted.
- [4] Greenwood R, Luckham PF: Minimising the viscosity of concentrated dispersions by using bimodal particle size distributions, Colloids and Surfaces 144 (1998) 19-147.
- [5] Chong JS, Christiansen EB, Baer AD: Rheology of concentrated suspensions, Journal of Applied Polymer Science 15 (1970) 2007-2021,.
- [6] Hunt WJ, Zukoski C.F: The rheology of bimodal mixtures of colloidal particles with long-range, soft repulsions, Journal of Colloid and Interface Science 210 (1999) 343-351.
- [7] Sweeny H, Geckler RD: The rheology of suspensions. Journal of Applied Physics 25 (1954) 1135-1144.
- [8] Kemmere MF, Meuldijk J, Drinkenburgh AAH,

- German AL: Rheology and flow during high solids emulsion polymerisation of styrene, *Polym. React. Eng.* 6 (1998) 243-268.
- [9] Poslinski AJ, Ryan ME, Gupta RK, Seshadri SG, Frechette EJ: Rheological behavior of filled polymeric system II. The effect of a bimodal size distribution of particulates, *J. Rheol.* 32 (1988) 757-771.
- [10] Farris RJ: Prediction of the viscosity of multimodal suspensions from unimodal viscosity data, *Transactions of the Society of Rheology* 12 (1968) 281-301.
- [11] Horn FM, Richtering W: Viscosity of bimodal charge-stabilized polymer dispersions, *J. Rheol.* 44 (2000) 1279-1292.
- [12] Berend K, Richtering W: Rheology and diffusion of concentrated monodisperse and bidisperse polymer latices, *Colloids and surfaces A* 99 (1995) 101-119.
- [13] Greenwood R, Luckham PKF, Gregory T: The effect of diameter ratio and volume ratio on the viscosity of bimodal suspensions of polymer lattices, *J. Colloids Interf. Sci.* 191 (1997) 11-21.
- [14] Schneider M, Claverie J, Graillat C, McKenna T: High solids content emulsions. I. A study of the influence of the particle size distribution and polymer concentration on viscosity, *J. Applied Polymer Sci.* 84 (2001) 1878-1896.
- [15] Servais C, Jones R, Roberts I: The influence of particle size distribution on the processing of food, *Journal of Food Eng.* 51 (2002) 201-208.
- [16] Guyot A, Chu F: High solids content latexes with low viscosity, *Colloid Polym. Sci.* 279 (2001) 361-367.
- [17] Luckham PF, Ukeje MA: Effect of particle size distribution on the rheology of dispersed systems, *J. Colloid Interface Sci.* 220 (1999) 347-356.
- [18] Kim IT, Luckham PF: Some rheological properties of bimodal sized particulates, *Powder Technology* 77 (1997) 31-37.
- [19] Neuhausler S, Richtering W: Rheology and diffusion of concentrated sterically stabilized polymer dispersions, *Colloids and Surfaces A* 97 (1994) 39-51.
- [20] Tadros TF, Liang W, Costello BA, Luckham PF: Correlation of the rheology of concentrated dispersions with interparticle interactions, *Colloids and Surfaces A* 79 (1993) 105-114.
- [21] Pishvaei M, Graillat C, McKenna T, Cassagnau P: Rheological behaviour of polystyrene latex near the maximum packing fraction of particles, *Polymer* 46 (2005) 1235-1244.
- [22] Schmidt M: Rheological properties of suspensions with spherical particles in shear and elongational flows, *Appl. Rheol.* 11 (2001) 220-227.
- [23] Barnes HA: An appreciation and critique of the suspension rheology research of Vladimir Vand, *Appl. Rheol.* 10 (2000) 248-253.
- [24] Ouchiya N, Tanaka T: Porosity estimation for random packings of spherical particles, *Ind. Eng. Chem. Fundam.* 23 (1984) 490-493.
- [25] Pal R: Relative viscosity on non-Newtonian concentrated emulsions of noncolloidal droplets, *Ind. Eng. Chem. Res.* 39 (2000) 4933-4943.
- [26] Saethre B, Thorjussen T, Jacobsen H, Pedersen S, Leth-Olsen K-A: Improved plastisol flow and reduced level of plasticiser in paste PVC formulations, *Plastics, Rubber and Composites* 28 (1999) 170-174.
- [27] Espiard P, Peres R, Soares C, Ernst B: Rheology of poly(vinyl chloride) plastisols, *Plastics, Rubber and Composites Processing and Applications* 26 (1997) 153-156.
- [28] Nakajima N, Harrell ER: Rheology of PVC plastisol: particle size distribution and viscoelastic properties, *Journal of Colloid and Interface Science* 238 (2001) 105-115.
- [29] Garcia JC, Marcilla A: Study of the flow properties and the ageing process in PVC plastisols from commercial PVC resins, *Eur. Polym. J.* 33 (1997) 753-759.
- [30] Collins EA, Hoffmann DJ: Rheology of PVC dispersions: I - Effect of particle size and particle size distribution, *Journal of Colloid and Interface Science* 71 (1979) 21-29.
- [31] Laun HM, Bung R, Schimdt F: Rheology of extremely shear thickening polymer dispersions (passively viscosity switching fluids), *J. Rheol.* 35 (1991) 999-1034.

