

RHEOLOGY OF WET PASTES OF PVC PARTICLES

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ABSTRACT:

The present work deals with the study of the rheological behaviour of PVC (polyvinylchloride) pastes containing particles of $\approx 150 \mu\text{m}$ in diameter obtained by polymerization in suspension. The rheological properties of the PVC pastes were characterized by creep experiments using 6-bladed vane geometry. The pastes show a very small compliance and a very narrow linear domain. The effects of temperature, of interstitial liquid and of saturation level of the wet paste were studied in detail and it was found that they significantly modify the creep behaviour. Other techniques allowed us to characterise rearrangements of the particles under load, in compression, by their oedometric modulus and by the failure stresses measured using a shear box. A very high oedometric modulus was measured (20 MPa) and by application of the Mohr-Coulomb criterion the internal friction coefficient ($\mu \approx 0.6$) and the cohesion of the materials were deduced. We conclude from this investigation that the interfacial properties of the grains play a major role in the behaviour of the wet pastes under shear or in compression. The paper illustrates the difficulties in measuring the rheological and the structural properties of jammed systems made from non-ideal (real) particles and reveals the key parameters in studying such media.

ZUSAMMENFASSUNG:

Diese Arbeit befasst sich mit dem rheologischen Verhalten von Polyvinylchlorid (PVC)-Pasten, die Partikel mit einem Durchmesser von $\approx 150 \mu\text{m}$ enthalten und durch Suspensionspolymerisation hergestellt wurden. Die rheologischen Eigenschaften dieser PVC-Pasten wurden mit Kriechexperimenten unter Verwendung einer 6-Flügelgeometrie charakterisiert. Die Pasten besitzen eine sehr geringe Nachgiebigkeit und einen sehr kleinen linearen Bereich. Der Einfluss der Temperatur, der Porenflüssigkeit und des Sättigungsniveaus der nassen Paste wurde detailliert untersucht. Diese Parameter beeinflussen wesentlich die Kriecheigenschaften. Die Anwendung weiterer Techniken erlaubte, die Anordnung der Partikel unter Belastung und Kompression durch ihren oedometrischen Modul und durch ihre Versagensspannungen in Scherung zu charakterisieren. Ein sehr hoher oedometrischer Modul (20 MPa) wurde gemessen und der Koeffizient der inneren Reibung ($\mu \approx 0.6 \text{ mm}$) sowie die Kohäsion der Materialien durch Anwendung des Mohr-Coulomb-Kriteriums abgeleitet. Wir schliessen aus diesen Messungen, dass die Grenzflächeneigenschaften dieser Körner eine grösse Rolle bzgl. des Verhaltens der feuchten Pasten in Scherung oder in Kompression spielen. Der Artikel nennt die Schwierigkeiten bei der Messung der rheologischen und strukturellen Eigenschaften der blockierten Systeme, die aus nichtidealen (realen) Partikeln bestehen, und stellt die wesentlichen Parameter dar.

RÉSUMÉ:

Cette étude porte sur le comportement rhéologique des pâtes humides constituées de particules de PVC poly(chlorure de vinyle), dont les dimensions sont de l'ordre de $150 \mu\text{m}$ et qui sont obtenues par polymérisation en suspension. Les propriétés rhéologiques des pâtes de PVC ont été évaluées par des mesures en fluage à l'aide d'une géométrie à ailettes à 6 pales. Les pâtes ont une très faible complaisance et un domaine de linéarité très réduit. L'effet de la température, du choix du liquide interstitiel et du degré de saturation a été étudié et les résultats montrent que ces paramètres jouent un rôle important dans le comportement des pâtes. Nous avons également caractérisé les réarrangements des particules sous des charges croissantes en compression, par leur module œdémétrique et par leurs contraintes seuil de fracture à l'aide d'une boîte de cisaillement. Nous avons trouvé un module œdémétrique très élevé (20 MPa) et en appliquant le critère de Mohr-Coulomb nous avons déterminé le coefficient de friction interne ($\mu = 0.6$) et la contrainte de cohésion de ces milieux. En conclusion de cette étude, il apparaît que les propriétés interfaciales des grains jouent un rôle très important dans le comportement de pâtes sous cisaillement ou en compression. Cet article montre les difficultés de mesure des propriétés rhéologiques et structurales de systèmes coincés, formés de particules réelles et met en évidence les paramètres clef pour leur étude.

KEY WORDS: PVC, wet paste, jammed systems, creep, failure, oedometric modulus, shear box, saturation effects

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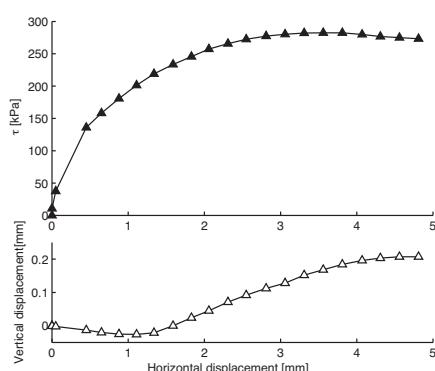
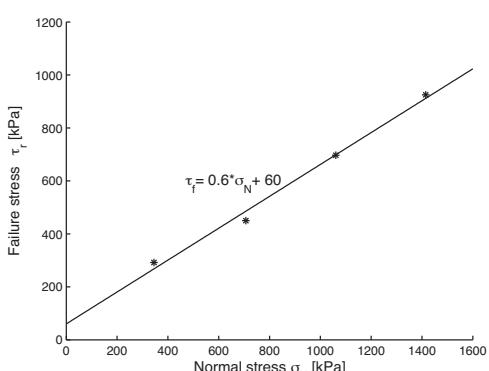


Figure 13 (left):
Mohr-Coulomb criterion for shear test.

Figure 14:
Shear stress and dilatancy of a PVC paste, $\sigma_N = 375 \text{ kPa}$, $U = 5 \text{ mm/min}$.

stresses: $\sigma_N = 357, 707, 1061$, and 1415 kPa with a fixed displacement rate $U = 3 \text{ mm/min}$. The tangential stress for fracturing is reached at the maximum of the curves as indicated by the arrows in Figure 12. Sample failures occur at this horizontal displacement.

Internal friction coefficient and cohesion

The failure stress τ_f is represented following the Mohr-Coulomb theory Figure 13 versus the normal stress σ_N obtained from Figure 12. After interpolation of the results and extrapolation to the zero normal stress, we obtain a friction coefficient $\mu = 0.6$ (friction angle $\alpha = 31^\circ$) and a cohesion $c = 60 \text{ kPa}$. Other experiments (data not shown) performed at various displacement rates U established that the internal friction coefficient $\mu = 0.6 \pm 0.04$ was independent of the shear velocity. Some friction coefficients known in the literature are: teflon against teflon $\mu = 0.04$, polystyrene against polystyrene $\mu = 0.5$, rubber against asphalt $\mu = 0.6 - 0.85$, which show that the friction coefficient between humid PVC grains is among the highest. The cohesion stress c determined by the extrapolation procedures varied between 15 and 60 kPa, consequently determination of this parameter should be verified by performing more measurements at low normal stresses.

Dilatancy

In order to observe the dilatancy phenomenon, the PVC paste must be well compacted. The shear of a material under compression is accompanied by particle disentanglement and thus a change in volume; dilatancy is the expansion of the material. The movement of grains leads to a decrease in the volume fraction during deformation. The first to highlight this phenomenon was OB Reynolds in 1885 [16]. The precise dilatancy effects depend on the initial conditions. In the shear box, efforts to detect such an expansion require ensuring, first, that PVC particles do not escape from the two half-boxes so as to preserve the solid mass of the sample. We present in Fig-

ure 14 an experiment which shows dilatancy of a sample sheared at $U = 5 \text{ mm/min}$ which was compacted at $\sigma_N = 375 \text{ kPa}$. Note that the curve starts with contraction before the expansion. This contraction is explained by an initial rearrangement of particles in which the volume fraction increases slightly. Then, PVC grains disentangle from each other and induce a dilation mechanism which is observed far from the shear plane.

Failure of granular media was investigated numerically using discrete element methods (DEM). Two-dimensional simulations were performed on polydisperse systems of elastic spheres by Thornton and Zhang [17]. Simulations clearly show a narrow zone, approximately 10 particles wide, where a shear band is located. Numerical simulations provide a very useful support for interpreting the behaviour of model systems and should be developed. To understand the fracture of wet granular media of real systems, like ours, it would be interesting to consider the particles surface roughness and the presence of a liquid at saturation and to analyse the changes that appear in the shearing patterns compared to those of model systems.

4 CONCLUSION

The aim of this investigation was to characterize the rheological and structural properties of wet dense pastes of PVC grains; these are non spherical particles, irregular in shape and their surfaces are coated with various dispersing agents (PVA type) which are amphiphilic molecules. Creep experiments establish that PVC pastes have a very low compliance and a very high viscosity, $10^8 - 10^9 \text{ Pa}\cdot\text{s}$. The influence of various physical and chemical parameters was analyzed: it was found that the degree of saturation is particularly important; temperature has an unexpected effect, the paste is more rigid when temperature is increased, even within a narrow range of temperatures ($20 - 50^\circ\text{C}$); in the non-saturated pastes, demineralised water or water from the slurry behave differently.

Oedometric measurements quantify the resistance of the saturated paste to compression under high loads. It was clear that the limit volume fraction ϕ_{RCP} was reached only after a long time and a high pressure. The paste was fractured in the shear box. The application of the Mohr-Coulomb criterion allowed us to determine the internal friction coefficients ($\mu \approx 0.6$) and the cohesion of the materials. The internal friction was found independent of the shear rate. The interstitial liquid appears to play a crucial role as modulating the mechanical properties of these pastes composed of non-colloidal particles. This is an incentive to explore the physical and chemical effects related to the nature of interfaces more precisely. As for modelling, numerical simulations of the non ideal systems, like the PVC grains, should provide a more detailed picture of the mechanisms of creep, fracturing or compression of this type of material.

REFERENCES

- [1] Coussot P: Rheometry of pastes, suspensions and granular materials, John Wiley and Sons (2005).
- [2] Allsopp MW, Vianello G: Vinyl chloride polymers, Encyclopaedia of Polymer Science and Technology (2002).
- [3] Burgess RH: Manufacture and Processing of PVC, Appl. Sci. Publishers (1982).
- [4] Saeki Y, Emura T: Technical progresses for PVC production, Prog. Polym. Sci. 27 (2002) 2055-2131.
- [5] Leung W-F.W: Industrial centrifugation technology, McGraw Hill, New York (1998).
- [6] Sherwood JD, Meeten GH: The use of the vane to measure the shear modulus of linear elastic solids, J. Non-Newt. Fluid Mech. 41 (1991) 1001-118
- [7] Baravian C, Lalante A, Parker A: Vane rheometry with a large, finite gap, Appl. Rheol. 12 (2002) 81-87.
- [8] Nguyen QD, Boger DV: Yield stress measurement for concentrated suspensions, J. Rheol. 27 (1983) 321-349.
- [9] Nguyen QD, Boger DV: Direct yield stress measurement with the vane method, J. Rheol. 29 (1985) 335-347.
- [10] Roos H, Bolmstedt U, Axelsson A: Evaluation of new methods and measuring systems for characterisation of flow behaviour of complex foods, Appl. Rheol. 16 (2006) 19-25.
- [11] Groger T, Tütün U, Heyes D M: Modelling and measuring of cohesion in wet granular materials, Powder Tech. 133 (2003) 203-215.
- [12] Dauchot O, Marty G, Biroli G: Dynamical heterogeneity close to the jamming transition in sheared granular media, Phys. Rev. Lett. 95 (2005) 265701.
- [13] Adamson AW: Physical chemistry of surfaces, J. Wiley and Sons, New York (1990).
- [14] Asmatulu R: Improving the dewetability characteristics of hydrophobic fine particles by air bubble entrapments, Powder Tech. 186 (2008) 184-188.
- [15] Andersen NPR, Christensen ML, Keiding K: New approach to determining consolidation coefficients using cake filtration experiments Powder Tech. 142 (2004) 98-102.
- [16] Reynolds OB: On the dilatancy of media composed of rigid particles in contact, Phil. Mag. 20 (1885) 469-481.
- [17] Thornton C, Zhang L: Numerical simulations of the direct shear test, Chem. Eng. Tech. 26 (2003) 153-156.



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