

# RHEOLOGICAL CHARACTERIZATION OF CONCENTRATED NANOCCLAY DISPERSIONS IN AN ORGANIC SOLVENT

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## ABSTRACT:

Nanoclay dispersions in organic solvents are widely used in cosmetics for a variety of gels and creams, whose properties depend on the powder content and the processing method. The control of the shear applied during processing is therefore essential for achieving the required properties. This study demonstrates the utility of applying rheological measurements for characterizing cosmetic products based on nanoclays and relating their viscoelastic properties to end-use performances. In particular, a rheological characterization of bentonite dispersions in isododecane at different clay content and shear history is presented. For each inorganic content, both mixed samples and samples subjected to several calendaring runs were studied. The effect of shear and clay content on the viscoelastic properties was investigated by a combination of oscillatory shear experiments under small-deformation conditions and by X-Ray diffraction. The tested samples showed a gel-like behaviour with a final structure depending on the applied shear stress. By increasing the inorganic content in the dispersion, a reduction in the gel stability to a further shear application was observed. Two models, developed for colloidal gels, were used to fit the rheological results enabling to evaluate the microstructure and the degree of dispersion of the tested samples and to relate the colloidal structure to the elastic properties.

## ZUSAMMENFASSUNG:

Dispersionen von Nanoschichtsilikaten in organischen Lösungsmitteln finden eine große Anwendung im Bereich der Kosmetika bei zahlreichen Gelen und Cremes, deren Eigenschaften vom Pulvergehalt und den Verarbeitungsbedingungen abhängen. Daher spielt die Kontrolle der Scherdeformation während der Verarbeitung eine wesentliche Rolle, um die gewünschten Eigenschaften zu erzielen. Diese Studie zeigt, wie nützlich die Anwendung rheologischer Messungen zur Charakterisierung kosmetischer Produkte auf Basis von Schichtsilikaten und die Interpretation der viskoelastischen Eigenschaften bezüglich der Gebrauchseigenschaften sind. In dieser Arbeit wird eine rheologische Charakterisierung von Bentonit-Dispersionen in Isododekan mit unterschiedlichem Füllstoffgehalt und Scherdeformationsgeschichte vorgestellt. Für sämtliche Konzentrationen wurden sowohl die Mischungen als auch Proben getestet, die mehrfach kalandriert wurden. Der Einfluss der Scherung und des Füllstoffgehaltes auf die viskoelastischen Eigenschaften wurde mit Hilfe kombinierter Scheroszillationsexperimente bei kleiner Amplitude und Röntgenstreuung untersucht. Die untersuchten Proben wiesen ein gelartiges Verhalten mit einer (End-)Struktur auf, die von der Spannung während der Deformation abhing. Durch Erhöhung des Bentonit-Anteils wurde eine Erniedrigung der Stabilität des Gels bei weiterer Scherung beobachtet. Zwei Modelle, die für kolloidale Gels entwickelt wurden, wurden an die rheologischen Resultate gefittet, um die Mikrostruktur und den Grad der Dispergierung der Materialien zu evaluieren und die kolloidale Struktur zu den elastischen Eigenschaften in Beziehung zu setzen.

## RÉSUMÉ:

Les dispersions d'argile nanométrique dans des solvants organiques sont largement utilisées dans l'industrie cosmétique pour la formulation d'une variété de gels et crèmes dont les propriétés dépendent de la méthode de mise en œuvre et de la quantité de poudre utilisée. Le contrôle du cisaillement appliqué durant le procédé de mise en œuvre est donc essentiel afin d'obtenir les propriétés requises. Cette étude démontre l'intérêt que présente l'utilisation de mesures rhéologiques pour caractériser les produits cosmétiques contenant des argiles nanométriques, et pour mettre en rapport leurs propriétés viscoélastiques avec les performances du produit final. En particulier, nous présentons la caractérisation rhéologique de dispersions de bentonite dans de l'isododécane possédant des concentrations en argile et des histoires de cisaillement variées. Pour chaque composition en produit inorganique, les échantillons mélangés et les échantillons soumis à plusieurs procédés de calendrage ont été étudiés. L'effet de la quantité de cisaillement et d'argile sur les propriétés viscoélastiques a été exploré en utilisant des expériences de cisaillement oscillatoire sous condition de petite déformation et des expériences de diffraction des rayons X. Les échantillons testés ont présenté un comportement de type gel avec une structure finale qui dépend de la contrainte de cisaillement appliquée. En augmentant la quantité d'inorganiques dans la suspension, une réduction de la stabilité du gel par rapport à l'application successive d'un cisaillement a été observée. Deux modèles, développés pour des gels colloïdaux, ont été utilisés pour ajuster les résultats rhéologiques, ce qui a permis d'évaluer la microstructure et le degré de dispersion des échantillons testés, et de relier la structure colloïdale aux propriétés élastiques.

**KEY WORDS:** nanoclay, gel, rheology, viscoelastic properties, cosmetics, calendaring

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bone relating the particle volume fraction with aggregate size. Likewise, the critical strain value can be related to the volume fraction as follows:

$$\gamma_{crit} \propto \phi^{-(1+x)/(3-d_f)} \quad (3)$$

The linear regression of the plots in Figure 8 provide the power law exponents with which Eqs.2 and 3 are solved simultaneously to give the values reported in Table 4. It should be noted that, in order to obtain reliable plots in Fig. 8, strain sweep measurements of dispersions with intermediate clay content ( $\phi = 6.5\%$ ) have been carried out.

The values of the extracted fractal dimensions ( $d_f$ ) are comparable with those obtained for clay networks in hydrophobic polymers such polypropylene or polystyrene [30]. The  $d_f$  values are in agreement also with those obtained for clay networks in water and for colloidal gels made out of non-spherical colloids [31 – 32]. The fractal dimension of aggregates formed by slow aggregation has been shown to be quite universal for various colloidal particles, ranging from colloidal golds to colloidal silica and to colloidal polystyrene particles [33]. The effect of shear application by calendaring produce an increase in the backbone dimension  $x$  but a very slight decrease in the fractal dimension  $d_f$ .

From the obtained results it appears that two factors contribute to the structural evolution of bentonite-isododecane dispersions: the orientation of the tactoids and the aggregation due to strong thermodynamic interactions. The attractive inter-particle forces create a more uniform particle network, whose elasticity and stability is enhanced by consecutive application of high shear forces as long as the clay content is below a threshold value. Above this critical value the further application of shear during processing of bentonite dispersions accelerates the gel breakdown with a consequent decay of mechanical properties. The viscoelastic characterization here presented can be very helpful for quality control. In order to reach the desired gel elasticity, it can be successful to use a powder content below the critical threshold and apply shear through subsequent calendaring runs. The optimum combination of content and shear can be adapted to meet the required end-use performance.

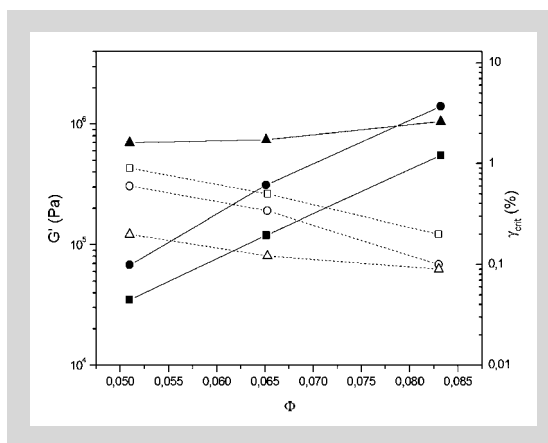


Figure 8: Shih et al. model plots showing the storage modulus (filled symbols) and the critical strains (open symbols) as a function of clay volume fraction (■: mixed samples, ●: once calendared samples, ▲ twice calendared samples).

## 5 CONCLUSIONS

The work has demonstrated the utility of applying rheological measurements for characterizing the viscoelastic behaviour of cosmetic nanofilled gels, obtained by dispersion of bentonite powder in isododecane. The tested samples have shown a gel-like behaviour with a final structure dependent on the clay content and shear history applied by the processing method (mixing or mixing and calendaring).

The calendaring produces a good degree of dispersion of the nanoclay in the solvent, as also confirmed by the X-Ray diffraction patterns. Nevertheless, the repeated calendaring runs can cause the formation of particle-particle and particle-solvent aggregates of different size and different structural level, thus accelerating the structural sample breakdown by further shear application. This phenomenon is strictly dependent on the clay content in the dispersion as also demonstrated by the reduction of the critical strain. The dynamic mechanical results have been interpreted by using the models proposed by Gabriele et al. and by Shih et al.. The investigation presented in this paper, based on easy and fast measurements under small deformation conditions, can be used to determine the proper clay content for nanofilled gel formulations in order to enhance their stability under manufacturing and storage conditions.

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