DYNAMIC MECHANICAL FREEZING POINTS OF COSMETIC O/W EMULSIONS AND THEIR STABILITY AT LOW TEMPERATURES

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Abstract

To develop cosmetic products quickly and effectively, developers need reliable test methods for evaluating product stability. Phenomena that determine the stability of cosmetic emulsions include phase transitions taking place in the relevant application and storage temperature range. The tendency of ingredients to crystallize influences the stability of emulsions especially at low temperatures. In this article a Differential Scanning Calorimetry (DSC) was used to determine the temperature of the water/ice phase transition of the continuous water phase for oil in water emulsions. A rheological, oscillating test method was developed to measure the phase transition temperature and the results were compared with those of the DSC and standard cold storage tests. There was a correlation of the crystallization temperature of the external water phase with the storage stability at –10°C. The accompanying increase in viscosity with cold storage due to structural alteration of the emulsions could be confirmed by TEM micrographs.

Zusammenfassung

Für eine schnelle und zielstrebige Entwicklung von stabilen kosmetischen Produkten ist es wichtig, dem Entwickler aussagekräftige Messmethoden für die Stabilitätsbeurteilung zur Verfügung zu stellen. Phänomene, die die temperaturabhängige Stabilität von kosmetischen Emulsionen beeinflussen sind u.a. Phasenübergänge, die im relevanten Anwendungs- und Lagertemperaturbereich stattfinden. Das Kristallisationsverhalten der Inhaltsstoffe beeinflusst besonders bei tiefen Temperaturen die Stabilität der Emulsionen. In diesem Artikel wird an Öl in Wasser-Emulsionen die Temperatur des Phasenübergangs Wasser/Eis der kontinuierlichen Wasserphase mit Hilfe der Differential Scanning Calorimetry (DSC) bestimmt. Eine rheologische, oszillierende Messmethode wird zur Ermittlung der Phasenübergangstemperatur entwickelt und die Resultate mit denen der DSC- und standardisierten Kälte-Lagerungstests verglichen. Ein Zusammenhang zwischen Kristallisationstemperatur der äußeren Wasserphase und der Stabilität bei -10°C Lagerung wird aufgezeigt. Das Einhergehen von Viskositätserhöhung bei Kältelagerung aufgrund struktureller Veränderungen der Emulsionen wird durch TEM Aufnahmen belegt.

Résumé

Afin de permettre un développement rapide et efficace de produits cosmétiques, les développeurs requièrent des tests fiables pour évaluer la stabilité des produits. Les phénomènes déterminant la stabilité des émulsions cosmétiques sont entre autres les changements d'état qui ont lieu dans les domaines usuels de température d'utilisation et de stockage. L'affinité des composants à cristalliser influence la stabilité des émulsions, particulièrement à basse température. Dans cette étude la technique par calorimétrie différentielle (Differential Scanning Calorimetry – DSC) a été utilisée pour déterminer la température de transition liquide/glace de la phase continue aqueuse pour des émulsions huile/eau. En outre un test rhéologique par oscillation a été développé pour mesurer la température de changement d'état et les résultats sont comparés à ceux obtenus par DSC et aux tests de stabilité standardisés de stockage à froid. Une corrélation entre la température de cristallisation de la phase aqueuse et les mesures de stabilité pendant le stockage à -10°C a été mise en évidence. L'accroissement de la viscosité durant le stockage à froid en raison de l'altération des émulsions a pu être confirmé par imagerie TEM.

1 INTRODUCTION

A wide variety of cosmetic emulsions are used as bases for skincare products for healthy and diseased skin. Therefore these products can range in consistency from a cream to a lotion or milk and even a fluid. In this market segment, innovation is the key to successfully meeting the customers' needs. Since today's trends are increasingly short-lived, a manufacturer of cosmetic products needs to respond quickly to new market demands. This means that development times must be drastically reduced while maintaining the same high product quality.

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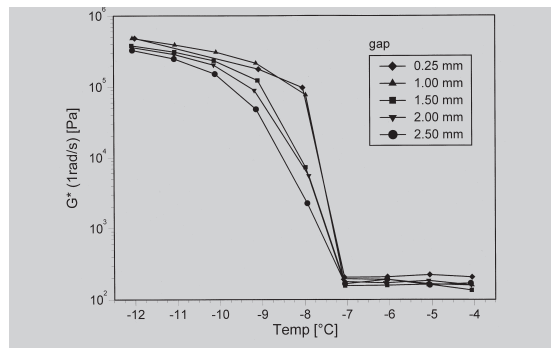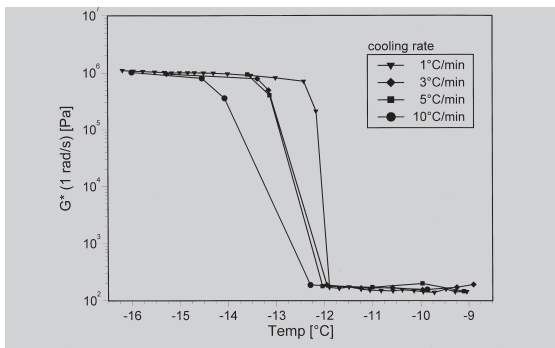
and that crystallization depends on the condition of the contact surface [6], overcooling should not be as pronounced in the rheological experiments. In these measurements the filling volume is 25 times larger and the surface of the measuring geometry coming into contact with the emulsion 50 times larger. In addition, the system is never fully at rest due to the applied dynamic mechanical oscillation. The results of the rheological measurement show no dependence on the frequency of the applied oscillation. The phase transition of the water phase takes place at a temperature that is 10 °C higher than in the DSC measurements. These crystallization temperatures are much closer to the real situation and therefore much more practice-oriented although still not free of crystal growth inhibition. The rheological determination of freezing points gives results that are clearly more reproducible than with the DSC method, and samples can be distinguished on the basis of the crystallization temperatures.

3.4 TEM MICROGRAPHS

Figure 5 shows a TEM micrograph of Emulsion D after one week of storage at room temperature. A clearly delineated oil phase (A) can be seen within the continuous water phase (B). Figure 6

shows the same emulsion after one week of storage at –10°C. Here the structure has been clearly altered with the previously delineated oil phase now more finely dispersed in the continuous water phase. Also clearly recognizable is the segregation pattern [8] of ice crystals (C) arising from the slow freezing process at –10°C. Water's tendency to form pure ice crystals results in an accumulation of dissolved and undissolved ingredients at the phase interface. The material accumulating there is compressed and can form a new three-dimensional structure. Both structural changes – ice crystal formation and interfacial structures – should be reflected in altered physical properties.

3.5 CORRELATIONS

In Figure 7 the rheological freezing points and the viscosity increases after storage at –10°C are plotted for samples B, C and D. Emulsion D, which has the lowest rheological freezing point, shows the smallest viscosity increase after cold storage. It can be seen that the lower the freezing point of the emulsion, the smaller the viscosity increase is after cold storage at –10°C.

Since the formulas of the samples stored at room temperature and in the cold are the same (no freezing point lowering additives), the
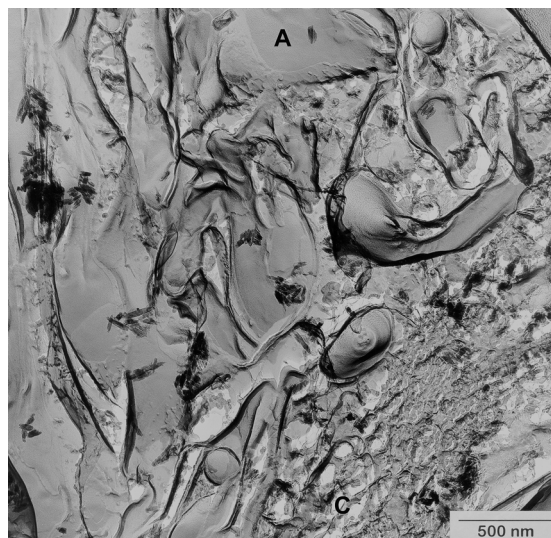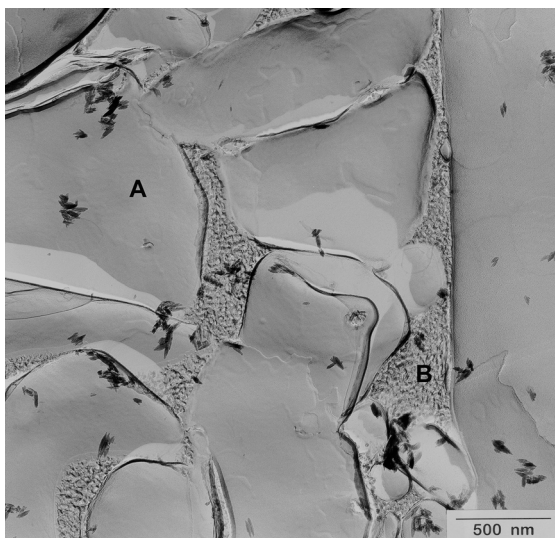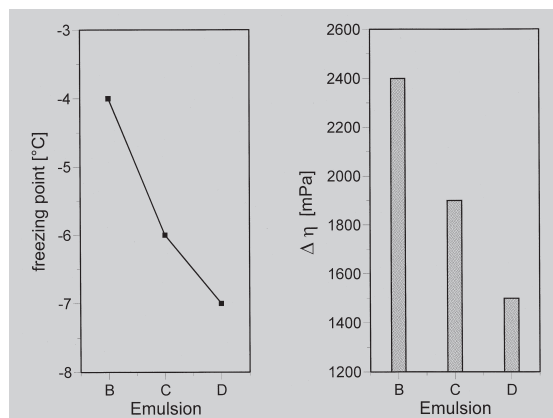
increased viscosity can only be explained by a change in the structure of the emulsions. Comparison of the TEM micrographs of the emulsions before and after cold storage reveals very different structures. The samples stored at room temperature have a relatively coarse structure with large areas of oil enclosed in the continuous water phase (see Figure 5). Following one week of cold storage a completely different, finer structure is present (see Figure 6). The previously large-area oil regions have broken up after storage at –10°C. Also clearly discernible are the segregation patterns [8] of ice crystals arising from the slow freezing at –10°C. The altered structure correlates with the altered physical properties of the emulsion after storage at –10°C. The denser pseudo-network of the more finely structured emulsion causes the increase in viscosity.

4   SUMMARY

It could be shown that the crystallization temperatures measured for the external phase of O/W emulsions with DSC are not reproducible. The problems associated with the measurement of the crystallization temperature can be largely avoided in the dynamic mechanical oscillation test. The rheological test method for determination of the freezing point provides reproducible results. These correlate with the viscosity changes determined in one-week storage tests at –10°C. There was a correlation of the crystallization temperature of the external water phase with the storage stability at –10°C. The accompanying increase in viscosity with cold storage due to structural alteration of the emulsions could be confirmed by TEM micrographs.

Due to the correlation of the freezing point of cosmetic O/W emulsions with low temperature stability, the product developer can obtain additional information on the stability at low temperatures in a minimum of time. This additional information on the thermal properties of the water phase in a finished formulation on cold storage permits timely action and thus shortens the time needed to develop a marketable product.

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