

# Surfactant-Activated Microgels

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## ABSTRACT

We describe a new class of high efficiency nonionic (non-polyelectrolyte) microgel rheology modifiers comprising crosslinked amphiphilic copolymers of alkyl acrylates and hydroxyalkyl esters that are activated by the available surfactant in personal care systems. Formulations containing less than 3wt% (% active) of these materials and anionic surfactants such as sodium dodecyl (lauryl) sulfate or sodium laureth sulfate display very uniform rheological properties over the broad pH range from 3 to 12. The materials also provide the unique property of high yield stress (greater than 1Pa at an oscillatory frequency of 1Hz) and strong shear thinning (viscosities lower than 2000mPa.s at  $3s^{-1}$ ) permitting suspension with easy pour.

**Keywords:** microgels, rheology modifiers, yield stress fluids, polymer-surfactant interactions

## 1 INTRODUCTION

Microgels are widely used as rheology modifiers in a variety of personal care products such as body washes, shampoos, skin creams, toothpastes and hair gels [1]. Typically, they comprise chemically crosslinked polymers with a pH-responsive functionality that is either base or acid sensitive. Free-flowing aqueous dispersions of these polymers are mixed with other ingredients in a formulation and then neutralized by the addition of a neutralizing agent such as an acid or a base. Upon neutralization, the polymers swell to form a randomly close-packed (jammed) network of swollen crosslinked particles imparting rheological features such as yield stress, viscosity, shear-thinning and optical clarity [2]. These features enable a certain flow profile as well as visually pleasing effects for the consumer such as suspension of beads and pearlescence. Well-known examples of pH-responsive microgel rheology modifiers are powdered Carbopol® polymers and alkali-swelling emulsion (ASE) polymers that contain a carboxylic acid moiety. A key feature of these materials is the large increase in diameter (or size) of individual crosslinked polymer particles when the pH is raised above the  $pK_a$  of the acid group. The high swelling efficiency allows formulators to achieve the desired yield stress and viscosity using relatively small amounts of polymer. Although highly effective, pH-responsive microgels suffer from the disadvantage that desired properties are obtained only over a relatively limited span of pH and, furthermore, significant changes in properties are observed in the range of pH values close to the  $pK_a$ . Crosslinked microgels with a

sulfonic acid group instead of a carboxylic acid group have been prepared in order to achieve uniform properties over a broader range of pH but these ionic microgels are not effective at the relatively high levels of surfactant commonly used in personal care formulations. It is also difficult for formulators to achieve a combination of high yield stress and strongly shear thinning (easy-pour) rheology with currently available materials. A major technical challenge is the development of efficient microgel polymers that provide uniform rheology and optical clarity over a broad pH range while enabling high yield stresses (for long-term bead suspension and pearlescence) and tunable viscosities in surfactant-containing formulations.

Here we describe a new class of high efficiency nonionic (non-polyelectrolyte) synthetic microgel rheology modifiers comprising crosslinked amphiphilic copolymers of alkyl acrylates and hydroxyalkyl esters that are activated by the available surfactant in personal care systems. We discuss the mechanism of action of these materials in terms of swelling of individual polymer particles and surfactant-mediated interaction of the swollen microgels using dynamic light scattering (DLS) and dynamic rheology. We demonstrate that it is possible to tailor the composition of these materials to combine a high degree of swelling with the mechanical rigidity necessary to achieve a high yield stress.

## 2 METHODOLOGY

Crosslinked copolymer microgels of alkyl acrylates and hydroxyalkyl esters were prepared by standard emulsion polymerization techniques. Stable suspensions were obtained containing about 30wt% solids in water.

The effect of surfactant on the mean particle size of microgel particles was determined by DLS. Measurements were made at 25°C using a Malvern® NanoZS system. The suspension of microgels was diluted to a concentration of 0.01wt% (% active) to minimize colloidal interactions and multiple scattering.

Dynamic rheology of mixtures of microgels and surfactants in water was measured at 25°C on an AR 2000ex rheometer from TA instruments with a cone and plate geometry (60mm diameter and 2° cone angle). The elastic ( $G'$ ) and viscous ( $G''$ ) moduli were determined as a function of increasing stress amplitude at a frequency of 1 Hz. The crossover of  $G'$  and  $G''$  was used to estimate the yield stress. Steady shear viscosities were measured over a shear rate range 0.05 to 500 $s^{-1}$ .

The percent light transmission (%T) of samples was measured using a Brinkmann® PC 910 colorimeter with a 420nm filter.

### 3 RESULTS AND DISCUSSION

Figure 1 shows the effect of surfactant (sodium dodecyl sulfate (SDS)) on particle size of a 0.01wt% aqueous suspension of a crosslinked polymer composed of ethyl acrylate, butyl acrylate, vinyl acetate and hydroxyethylmethacrylate in the presence of 0.02M sodium chloride. The particle diameter increases three-fold from 145 to 435nm as the surfactant concentration increases from 0 to 5.5mM. It is interesting to note that the particle size remains essentially unchanged until a surfactant concentration of about 1.3mM and displays a plateau above a concentration of about 3.5mM. The results suggest that expansion of microgels is driven by the association of surfactant micelles with the crosslinked polymer coils and electrostatic repulsion between the attached micelles. The association begins above a threshold concentration of surfactant known as the critical aggregation concentration (cac) and continues until all the available polymer is saturated with surfactant at which point there is no further increase in particle size.

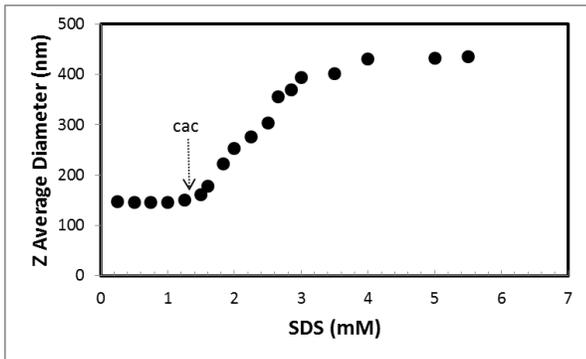


Figure 1: Effect of surfactant (SDS) on mean particle size of a cross-linked copolymer of ethyl acrylate, butyl acrylate, vinyl acetate and hydroxyethylmethacrylate in the presence of 0.02M sodium chloride. The polymer concentration is at 0.01wt%

The swollen microgels of Figure 1 interact with each other at concentrations above the overlap concentration ( $c^*$ ) to create a yield stress fluid with high optical clarity. Figure 2 shows the elastic and viscous moduli as a function of the oscillatory stress amplitude at a frequency of 1Hz for a sample containing 2.5wt% polymer and 3.2wt% (% active) SDS in water. The response is characteristic of the yielding behavior of soft glassy materials [3]. At low stress amplitudes, the microgels are in a randomly close packed (jammed) state and the material exhibits solid-like behavior ( $G' > G''$ ). As the amplitude

$\sigma$  of the oscillatory stress is increased, the material yields (i.e. the jammed network is broken) at  $\sigma = \sigma_y = 1.5\text{Pa}$ , where the yield stress  $\sigma_y$  is defined by  $G'(\sigma_y) = G''(\sigma_y)$ . Above  $\sigma_y$ ,  $G'' > G'$  and one observes liquid-like behavior. We have determined that a yield stress greater than 1Pa at a frequency of 1Hz is necessary for suspending beads and pearlescent agents such as mica particles. The high swelling efficiency shown in Figure 1 allows us to achieve this yield stress at relatively low concentrations of polymer.

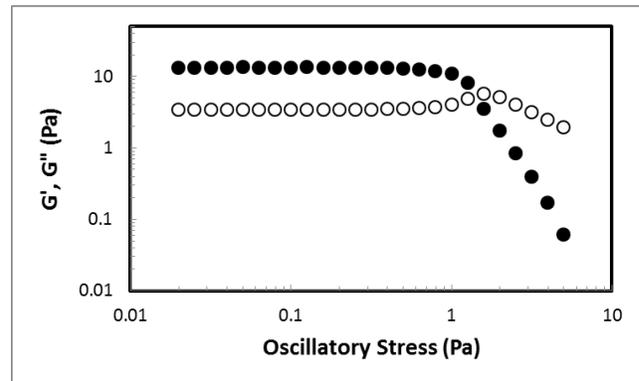


Figure 2: Elastic modulus (filled circles) and viscous modulus (open circles) versus the amplitude of oscillatory stress at frequency 1Hz of a formulation containing 2.5wt% of the polymer of Figure 1 and 3.2wt% SDS in water.

Figure 3 shows optical clarity (% T) and yield stress versus pH of a formulation containing 2.5wt% polymer (composed of ethyl acrylate, butyl acrylate, vinyl acetate and hydroxyethylacrylate), 12wt% (% active) sodium laureth sulfate (SLES2) and 2wt% cocamidopropyl betaine (CAPB). The inset shows suspension of 1.4mm sized beads of specific gravity 1.3 (Unisphere® REL551 from Induchem AG, Switzerland) after three months at room temperature. Both optical clarity and yield stress remain almost constant over the entire range of pH from 3 to 12 and this is reflected in the uniform suspension properties. Since properties are relatively invariant versus pH, no pH adjustment or neutralization is needed during formulation. As mentioned earlier, this feature along with the excellent surfactant compatibility are important advantages over currently available ASE rheology modifiers where pH has to be adjusted within a narrow band for optimum performance.

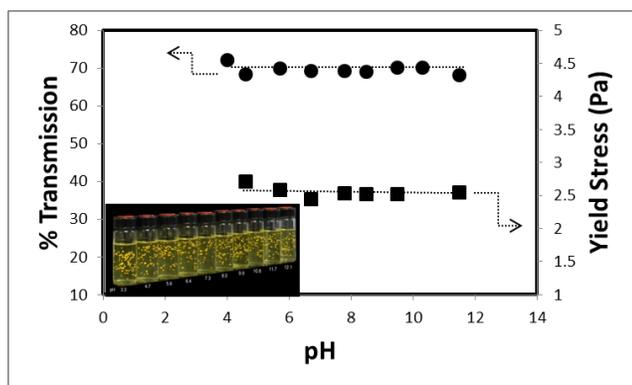


Figure 3: Optical clarity (percent light transmission) (filled circles) and yield stress (filled squares) versus pH of a formulation containing 2.5wt% polymer, 12wt% SLES2 and 2wt% CAPB in water. The inset shows suspension of beads versus pH for the same formulation

## 4 CONCLUSIONS

In summary, we have developed a new class of polymeric rheology modifiers for personal care products that we refer to as surfactant-activated microgels. The unique design of these nonionic materials provides large expansion (a factor of 3 in linear dimensions;  $3^3$  in volume fraction) by the available surfactant in personal care formulations. The swollen microgels interact to create a yield stress fluid at relatively low polymer concentrations providing uniform rheology and high optical clarity ( $> 70\%$  T) over a broad pH range without the need for neutralization. The new materials offer a significant advantage over currently available ASE rheology modifiers that demonstrate optimum properties (in terms of rheology and optical clarity) only in a narrow range of pH in surfactant containing systems.

## REFERENCES

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