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Effect of laponite clay particles on thermal and rheological properties of Pluronic triblock copolymer

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Special Chapter dedicated to the memory of dr. Michel Ollivon

Abstract The high concentration 17 wt% triblock copolymer poly(ethylene oxide)$_{100}$–poly(propylene oxide)$_{65}$–poly(ethylene oxide)$_{100}$ Pluronic F127 aqueous solutions with the addition of laponite is investigated as a novel temperature-sensitive hydrogel system. The critical micelle temperature (cmt) and the sol-to-gel transition were characterized by rheological experiments and differential scanning calorimetry. Experimental results showed that laponite particles have no significant influence on the cmt. On the other hand, viscoelastic measurements have highlighted an increase of the sol-to-gel transition temperature for mixtures with 2 and 3 wt% of laponite particles. This additive can be used to adjust the gelation temperature close to physiological temperature in medical applications.

Keywords Critical micelle temperature · DSC · Pluronic · Laponite · Rheology · Sol–gel transition

Introduction

Water soluble triblock copolymers of poly(ethylene oxide) (PEO) and poly(propylene oxide) (PPO) are well known as non-ionic polymeric surfactants [1]. The PEO–PPO–PEO copolymers are commercially known as Pluronics (manufactured by BASF) or Poloxamers (manufactured by ICI) and have attracted a great deal of attention due to their thermoreversible gel-like behaviour. A variety of techniques have been used to study the micelle formation, micelle structure and gelation of PEO–PPO–PEO copolymer solutions [2–5]. At low temperature both PPO and PEO are water soluble and the copolymer chains are fully soluble in aqueous solution. As the temperature increase, the PPO block becomes hydrophobic and when the concentration is larger than the critical micelle concentration, individual micelles begin to form with a PPO core and a PEO corona. Micellization at fixed concentration occurs above a critical micelle temperature (cmt) or at fixed temperature above a critical micelle concentration (cmc). At sufficiently high concentration, Pluronic copolymers are characterised by gel-type behaviour. The Pluronics are useful as biocompatible materials for biomedical and personal care applications where their gelation properties are exploited [3, 6, 7].

The gelation properties of thermosensitive hydrogels are widely used in several biomedical applications, such as drug and gene delivery [8], inhibition of tissue adhesion [9], burn wound covering [10, 11] and surfactants for emulsification of food and personal care products [12, 13]. By adjusting the composition, the molecular weight and the concentration, the reversible gelation can occur at physiological temperature [14].

An extensive number of studies have been devoted to the topic of complex interactions between polymers and solid colloidal particles [15–22]. Many of these works are driven by industrial interest, for example, the pharmaceutical, pulp and paper and petroleum industries.

However, there are few studies that have examined adsorption of Pluronics on clay particles, Hecht and Hoffmann [23] examined Pluronic adsorption on saponite and De Lisi et al. [24] presented a mechanism of

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interaction following which some segments of the adsorbed macromolecule are anchored to the laponite particles (laponite RD). Nelson and Cosgrove [25] studied the adsorption of selective Pluronics on laponite, but this study was performed on dilute solutions where the focus was elucidating the structure of the adsorbed copolymer chains.

Our aim in this study is to modify and control the rheological properties of associative gels by addition of laponite clay which is widely utilized in industry as rheological additive. This additive can be used to adjust the gelation temperature close to physiological temperature in medical applications. Laponite clays, which are disk shaped particles with a high aspect ratio, can be produced synthetically, with a low level of impurity and a reproducible particle size.

Experimental investigation on the thermo-rheological characterization of Pluronic F127 formulated with laponite RDS is presented in order to understand the modification of the thermal gelation of the copolymer and the influence of the concentration of added laponite particles on the gelation-process.

Materials and methods

Materials

The Pluronic copolymer used in these experiments is obtained from BASF Corp and is also used as received without further purification. The reported chemical structure for the Pluronic F127 is PEO_{100}, PPO_{65}, PEO_{100} (see Fig. 1) and its nominal molar mass is 12,600 $gmol^{-1}$.

Pluronic solution was prepared in ultrapure water (Millipore Elix 3), the mass fraction W_P was adjusted at 34% and the solution was left for 1 week at low temperature ($T = 0$ °C) to ensure full dissolution of the copolymer.

The synthetic clay used was laponite RDS from The Laporte Industries (Warrington, UK). Laponite RDS differs from the more widely used laponite RD due to the presence of a peptizing agent. The chemical formula of the laponite RDS is $Si_8MG_{85.45}LI_{0.4}H_4O_{24}Na_{0.7} + Na_4P_2O_7$. The size of particle is 30 nm diameter and 1 nm thickness. The peptizer $Na_4P_2O_7$ modifies the surface of the laponite platelet and increases its stability in aqueous dispersions. Therefore laponite RDS can form solutions at higher concentrations than laponite RD. Laponite dispersions are very sensitive to pH, for pH <9 laponite RD particles dissolve. In prior studies on laponite RD Mourchid et al. [26–28] showed that the laponite dispersions are stable at pH = 10, so our solutions were prepared under these alkaline conditions.

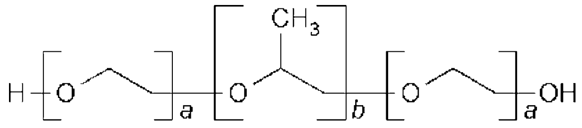

Fig. 1 Chemical structure of Pluronic F127 (a = 100 ethylene oxide portion, b = 65 propylene oxide portion)

The laponite dispersions was prepared by slowly adding powder to ultrapure water (Millipore Elix 3) adjusted at pH 10 the final mass fraction W_L of laponite dispersions were 2, 4 and 6%. The dispersions were left for several days until the clay was dispersed completely in water and forming a clear stable dispersions.

Mixtures were prepared by adding Pluronic solution to laponite dispersion of different concentrations, such that the final mass fraction of Pluronic defined as $W_P = m(F127)/[m(F127) + m(RDS) + M(water)] = 17$ wt%, and the mass fractions of laponite are defined as $W_L = m(RDS)/[m(F127) + m(RDS) + M(water)] = 1, 2$ and 3 wt%. The resulting dispersions were kept at 0 °C for 1 week and the final solutions were homogeneous and transparent.

Methods

Rheological measurements

For rheological characterization, Carrimed CSL100 stress-controlled rheometer was used. Measurements were performed using the cone and plate geometry (40 mm diameter, cone with 2° cone angle). A solvent trap containing water was used to ensure the volume fraction did not change. To measure G' and G'' (storage and loss modulus, respectively) as a function of temperature, a sweep test was carried out in the temperature range from 10 to 40 °C with a heating rate of 1 °C/min, at a fixed frequency of 1 Hz and a fixed stress of 0.1 Pa verified to be in the linear viscoelastic regime for all measurements. Several experiments were repeated on the same sample to test the reproducibility of the measurements: the data repeatability was ±1%.

Calorimetric measurements

Differential Scanning Calorimetry (DSC) measurements were carried out using a Mettler Toledo calorimeter. Samples ranging from 5 to 8 mg were loaded in hermetically sealed, aluminium crucibles pans, and a deionized water pan was used as a reference. The differential heat flow was recorded at a heating and cooling rate of 1 °C/min from −50 to 50 °C. Any weight losses were observed after thermal experiment. For the calibration, the latent heat of water and indium (purity 99.98%) were measured, and these measured values coincide with the reference values [29] within ±1.8%.

Results and discussion

Rheological analysis

Figure 2 shows the results of the temperature sweep test for the mixtures Pluronic F127–laponite RDS. When only a few laponite particles are dispersed in the solution (1 wt%), we show that the rheological behaviour of the mixture resembles that of the Pluronic F127. The influence of laponite appears for mixture containing 2 and 3 wt% laponite particles, the macroscopic properties are significantly affected by laponite particles. Then, we observed a sol-to-gel transition and three regions:

(i) First region, in which both G' and G'' are very small and $G'' > G'$, is liquid like dispersions.

(ii) Second region, in which both G' and G'' increase dramatically with temperature for all the concentrations, is soft gel. This abrupt increase of G' and G'' appears around $T = 30$ °C for 17 wt% Pluronic and 17 wt% Pluronic–1 wt% laponite mixture and around $T = 33$ °C for 17 wt% Pluronic–2 wt% laponite and 17 wt% Pluronic–3 wt% laponite mixtures. The temperature of gelation is determined when $G' = G''$, i.e. the transition between the rheological behaviour of a viscoelastic liquid ($G' < G''$) to a rheological behaviour of a viscoelastic solid ($G' > G''$). Figure 2 shows that the addition of laponite particles for concentrations above 1 wt% implies a shift in the gelation process to higher temperatures.

(iii) Third region, in which the G' and G'' increase very slightly with temperature, is hard gel.

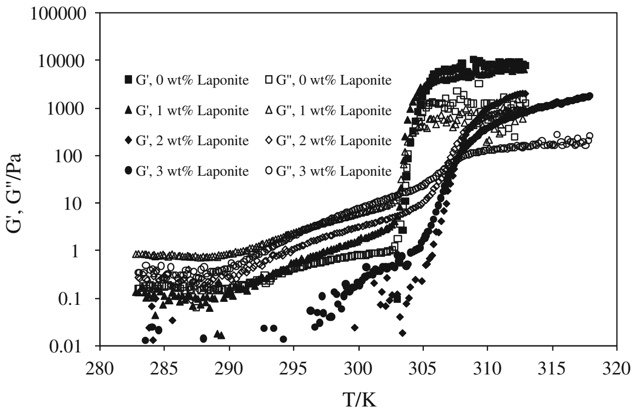

Fig. 2 Storage and loss modulus G', G'' at a frequency of 1 Hz and a stress of 0.1 Pa as a function of temperature, for the mixtures of Pluronic F127 (17 wt%) and laponite RDS: (*filled square*, *open square*) 0 wt%; (*filled triangle*, *open triangle*) 1 wt%; (*filled diamond*, *open diamond*) 2 wt%; (*filled circle*, *open circle*) 3 wt%

Analysis of critical micelle temperature

In rheological experiments, the critical micelle temperature (cmt) is defined as the temperature at which the solution viscosity is minimum. Figure 3 shows the variation of the viscous modulus as a function of temperature for the different mixtures. At low temperature, micelles have not yet formed and G'' decreases exponentially (linearly in the semilog plot) with T, due to the thermal motion of copolymer chains. When the cmt is reached, G'' begins to increase indicating the formation of micelles and the interaction between them [30]. Figure 3 shows that the mixtures seem to have the same value of cmt, this result will be confirmed more accurately by calorimetric measurements.

Calorimetric analysis

Several authors [1, 23, 31–33] have shown that differential scanning calorimetry (DSC) is an effective method which characterise the micellization event. An endothermic "phase transition" is observed and attributed to micelle formation.

Figure 4 shows a typical DSC curve of 17 wt% solution of F127 and mixtures of 17 wt% of F127 and 1, 2 and 3 wt% of laponite particles. The DSC curve shows an endothermic transition around the same temperature (18 °C) for all the solutions. The peak can be observed on heating or cooling of the systems and its maximum lies almost at the same position. The origin of the DSC peak was assumed to be caused by dehydration of the PPO groups with increasing temperature and was assumed to be in accordance with the value of the enthalpy for the micelle formation [34, 35].

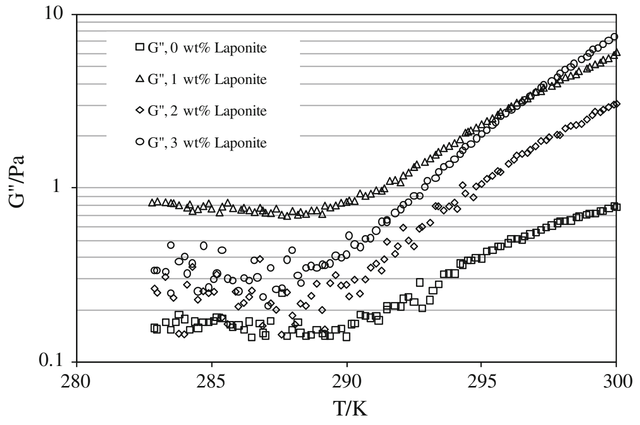

Fig. 3 Loss modulus G'' at a frequency of 1 Hz and a stress of 0.1 Pa as a function of temperature, for the mixtures of Pluronic F127 (17 wt%) and laponite RDS: (*open square*) 0 wt%; (*open triangle*) 1 wt%; (*open diamond*) 2 wt%; (*open circle*) 3 wt%

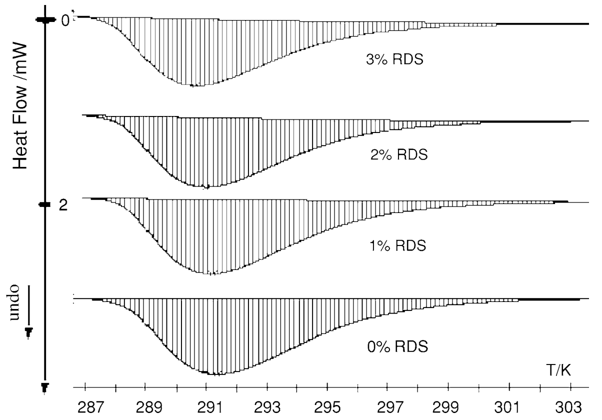

Fig. 4 DSC curve for the mixtures of Pluronic F127 (17 wt%) and laponite RDS (0, 1, 2 and 3 wt%)

Thermograms show that the micellization temperature of the Pluronic F127 is not significantly affected by the presence of the laponite particles.

Conclusions

The critical micelle temperature (cmt) and viscoelastic properties of aqueous Pluronic–laponite mixtures was investigated using oscillatory experiments and DSC calorimetry. The critical micelle temperature (cmt) was found around 18 °C for all mixtures, showing that laponite particles has no significant influence on the cmt. The mixtures exhibit: liquid viscoelastic behaviour ($G'' > G'$) at low temperature, with small values of G' and G''. Soft gel behaviour at intermediate values of temperature with dramatically increase of G' and G'', and hard gel behaviour at high temperatures with large values of G' and G'' ($G' > G''$). Thus, laponite particles can be used to increase the temperature of gelation for the Pluronic F127 copolymer. A decrease of almost an order of magnitude in the elastic and viscous modulus was observed with 2 and 3 wt% of added laponite particles.

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