

## Rheology of polyacrylamide/ layered double hydroxide nanocomposites

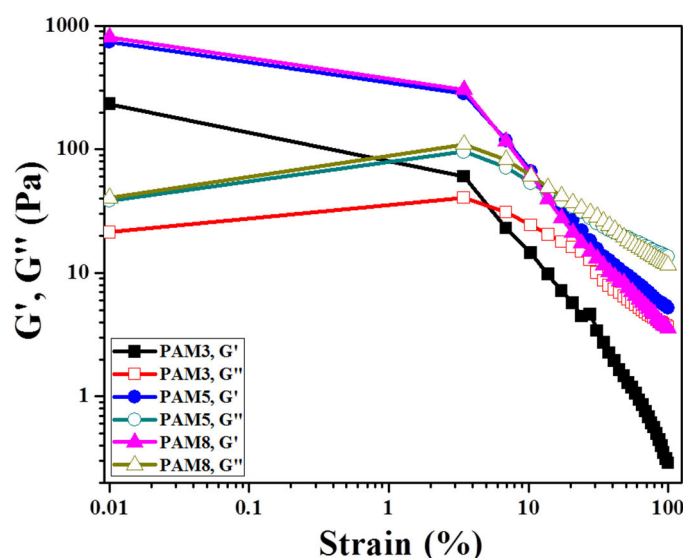
N'guadi Blaise Allou and Rajib Lochan Goswamee

*The viscoelastic properties and stability of hybrid gels, synthesized via in situ polymerization, are improved upon addition of magnesium-aluminum layered double hydroxide.*

Polyacrylamide (PAM) is a water-soluble polymer that exhibits good rheological behavior in aqueous dispersions. In recent years, PAM has thus received a substantial amount of interest for a variety of industry applications. For example, PAM is now used—to improve viscosity and solution rheology—in enhanced oil recovery operations.<sup>1,2</sup> For such applications, however, synthesis of high- or ultrahigh-molecular-weight PAM, as well as co-polymer hydrophobic association, are required for the chemical injection technique to be successful. These methods are therefore problematic for hydrolysis and at high temperatures, and are unsuitable for medium- and low-permeability oil reservoirs, as well as for conditions of low viscosity retention ratio and low solubility.<sup>3</sup>

Given these issues with the use of PAM for enhanced oil recovery, PAM-based nanocomposites (i.e., in which PAM is homogeneously mixed with inorganic nanoparticles) have also attracted considerable attention. Such nanocomposites may contain substances such as layered double hydroxide (LDH) or anionic clay. Indeed, these layered inorganic materials, which are widely used to modify the rheology of aqueous and non-aqueous systems,<sup>4,5</sup> are formed by a network of divalent and trivalent metal cations (i.e., sheets of hydroxide anions) with exchangeable anions between the layers. The preparation (via a simple solution dispersion procedure) of PAM/LDH nanocomposites has previously been reported, together with an evaluation of their stability and rheological properties.

In this study,<sup>6</sup> we therefore used a more advanced methodology to create an aqueous dispersion of PAM/LDH hybrid gels. Specifically, we used an in situ polymerization technique—with a magnesium/aluminum (Mg-Al) LDH formulation—to prepare the PAM/LDH hybrid gel aqueous dispersion. We have also conducted a thorough investigation into the structural, morphological, rheological, and thermal decomposition characteristics of the samples.



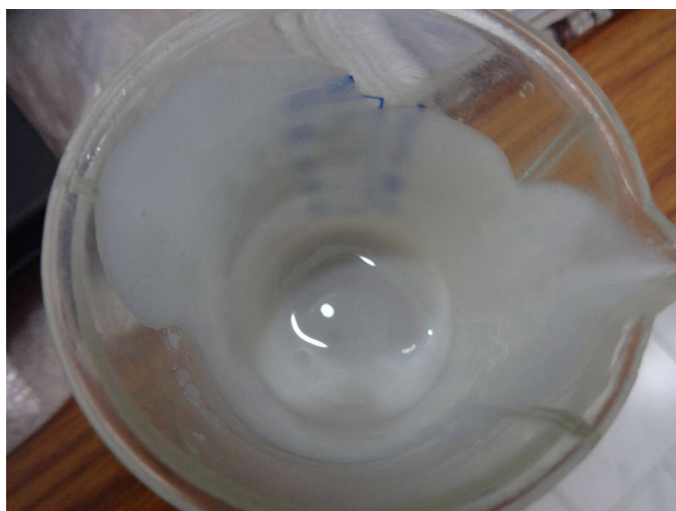
**Figure 1.** Results of amplitude sweep tests (conducted at an angular frequency of  $10\text{rad s}^{-1}$ ) for polyacrylamide (PAM) nanocomposites containing magnesium-aluminum (Mg-Al) layered double hydroxide (LDH) at concentrations of 3, 5, and 8%wt/v (PAM3, PAM5, and PAM8, respectively). The storage modulus ( $G'$ ) and loss modulus ( $G''$ ) results are shown as a function of strain.

For the first step of our nanocomposite fabrication approach, we prepared the Mg-Al LDH precursor by co-precipitation of the component hydroxides at constant pH, with the exchangeable carbonate anions in the gallery space.<sup>7</sup> Subsequently, we conducted the in situ polymerization synthesis of the nanocomposite in an LDH matrix. We then prepared an aqueous dispersion of acrylamide monomers and the Mg-Al LDH (at concentrations of 1, 3, 5, and 8%wt/v) in the presence of  $N,N,N',N'$ -tetramethylethylenediamine and ammonium persulfate. To do this, we performed sonochemical shaking (i.e., with a 2s pulse on

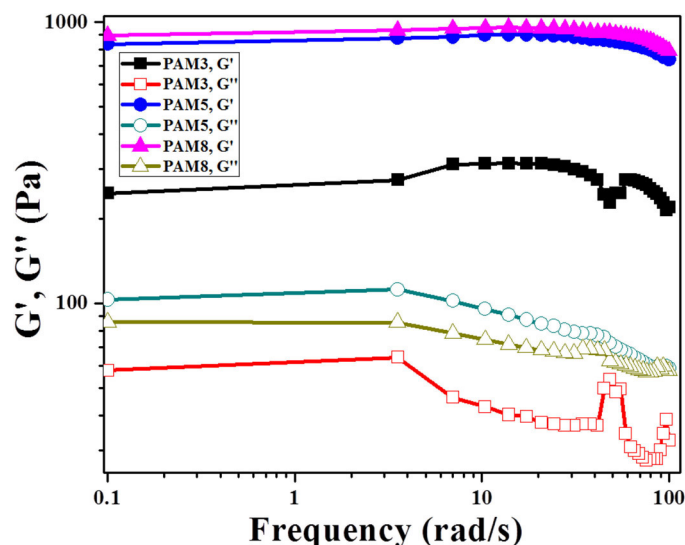
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and a 4s pulse off, at an amplitude of 33%) in a high-intensity ultrasonic processor, with a one-inch solid titanium horn, for 100 minutes and at 35°C. We then used a rheometer (with a rough parallel plate geometry, having a diameter of 25mm and a 0.5mm gap) to evaluate the rheological properties of our hybrid gels under oscillatory conditions. To determine the linear-viscoelastic (LVE) region for our samples, we submitted them to the parallel plate and increased the amplitude of oscillation to 100% apparent strain shear (to maintain an angular frequency of 10rad/s).

Our rheology measurements for the PAM suspension that contains no LDH, as well as for the PAM/LDH 1%wt/v suspension, indicate that these samples exhibit shear thinning behavior. In addition, from our amplitude sweep tests, we determined the storage modulus ( $G'$ ) and the loss modulus ( $G''$ )—representing the elastic and viscous behavior of the viscoelastic materials, respectively—as a function of the applied strain (see Figure 1). Our results show that in the LVE region (i.e., for a strain of <5%) for the PAM/LDH 3, 5, and 8%wt/v samples (PAM3, PAM5, and PAM8, respectively),  $G'$  is larger than  $G''$ . The intersection point between  $G'$  and  $G''$  marks the transition of the samples from being solid-like to liquid-like, and so the results indicate that our synthesized nanocomposites behave like a viscoelastic gel. This result is also evident with the naked eye, as can be seen in a photograph of one of our hybrid gels (see Figure 2). Beyond the transition point, both  $G'$  and  $G''$  for all three nanocomposites decrease sharply with increased strain. This is because of the breakdown of the structures in the hybrid gels. We also observed that increasing the LDH concentration from 3 to 5%wt/v caused an increase in both  $G'$  and  $G''$ , and a shift in the transition point from a strain of 5.06 to 11.09%. Our findings thus



**Figure 2.** Photograph showing a vial containing a synthesized PAM/Mg-Al LDH nanocomposite.



**Figure 3.** Results of frequency sweep tests (conducted at a shear strain of 1%) for the PAM3, PAM5, and PAM8 nanocomposites.

confirm the strong rheology-modification behavior of LDH. In contrast, we observed almost no change in either  $G'$  or  $G''$  by increasing the LDH to 8%wt/v.

Once we had determined the LVE region, we performed our frequency sweep tests in this region to measure the frequency dependency of  $G'$  and  $G''$ . We conducted these tests in triplicate at 25°C, from low to high frequency, and with a constant shear strain of 1%. From our results (see Figure 3), we observe that both moduli—for the PAM3, PAM5, and PAM8 samples—are nearly parallel with respect to frequency, and that  $G'$  is much greater than  $G''$  even at high angular frequencies. This behavior is typical of solid-like viscoelastic gels. Furthermore, we observe no crossover between  $G'$  and  $G''$ , which indicates the high stability and weak gel structure of the composites. Nonetheless, we found that the measured  $G'$  values for PAM5 and PAM8 were higher than for PAM3, which indicates the increased gel-like viscoelastic character and higher stability of the samples upon increased addition of LDH.

In summary, we have used an in situ polymerization method to prepare PAM/LDH hybrid nanocomposites. Our rheological measurements show that the viscoelastic properties of the samples were improved by the addition of Mg-Al LDH. Moreover, we find the solid-like and gel-like viscoelastic characteristics of the composites, as well as their stability, increased with higher LDH content. In our future work, we plan to analyze the rheological behavior of PAM composites that contain LDH-modified antibiotic molecules. It is hoped that these could one day be used as a slow-release medium in biomedical applications.

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