



The effect of organoclay concentration on polyurethane nanocomposites

Shirley Peng and Jude Iroh

Incorporating nanosized clay fillers into a polyurethane matrix improves the processability of the resultant composites at ambient temperatures.

Polyurethanes (PUs) represent an extremely versatile class of materials and have many desirable properties, including excellent flexibility and elasticity. These materials do, however, exhibit poor barrier properties, reducing their potential use as a protective coating. To overcome this issue, nanosized fillers, such as montmorillonite clay, can be incorporated into the matrix. Achieving good clay dispersion is key to obtaining a polymer composite with decreased permeability to gas and vapor.¹ This reduced permeability occurs due to the large aspect ratio and high surface area of the fully exfoliated clay platelets, which create a more tortuous pathway and decrease the movement of penetrant molecules. Additionally, introducing a network structure in the PU via increased chemical crosslinks results in a dense matrix with better chemical resistance.²

The properties of clay-reinforced crosslinked PU have been studied by several researchers, who have thus far primarily focused on characterizing the tensile strength and thermal stability of the resulting material. Their efforts have shown that the overall properties of these nanocomposites outperform pristine polymer.³⁻⁵ However, little attention has been focused on processability, which represents an important parameter for coating applications.

To investigate processability, we studied the effect of clay concentration and temperature on the rheological properties of branched PU in solution.⁶ When this solution is cured thermally, a 3D network structure is formed. Cloisite 30B clay was implemented as the filler due to its good compatibility with PU. We varied clay content between 0.5 and 10wt% and incorporated it in situ to ensure good dispersion of the silicate layers. Dilute solution and Brookfield viscometry were implemented to measure the approximate molecular weight and the viscosity, respectively.

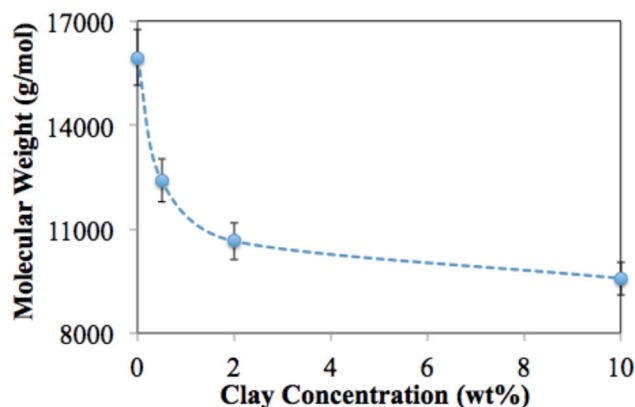


Figure 1. Dilute solution viscometry measurements showing the estimated molecular weight of polyurethane (PU) containing varied Cloisite 30B clay concentrations. Between 0 and 10wt%, the molecular weight ranges between $16,000 \pm 300$ g/mol and 9600 ± 100 g/mol, respectively.

The addition of clay results in a reduction of the molecular weight in the final polymer. In the 10wt% clay nanocomposite solution, we observed a 40% decrease in the molecular weight (see Figure 1). We also observed this effect in the rheological measurements performed on the neat PU and the PU nanocomposite solutions at 25 and 70°C: see Figure 2(a) and (b). The overall viscosities of the nanocomposites were significantly lowered, indicating improved processability in the material.

We believe that the disparity in average molecular weight occurs as a result of dispersed clay platelets obstructing the contact between monomers during polymerization. Because the reactive sites are blocked, the monomers would require longer reaction times to build up their polymer chains. This assumption correlates well with rheological measurements obtained at varied temperatures. Because polymers

Continued on next page

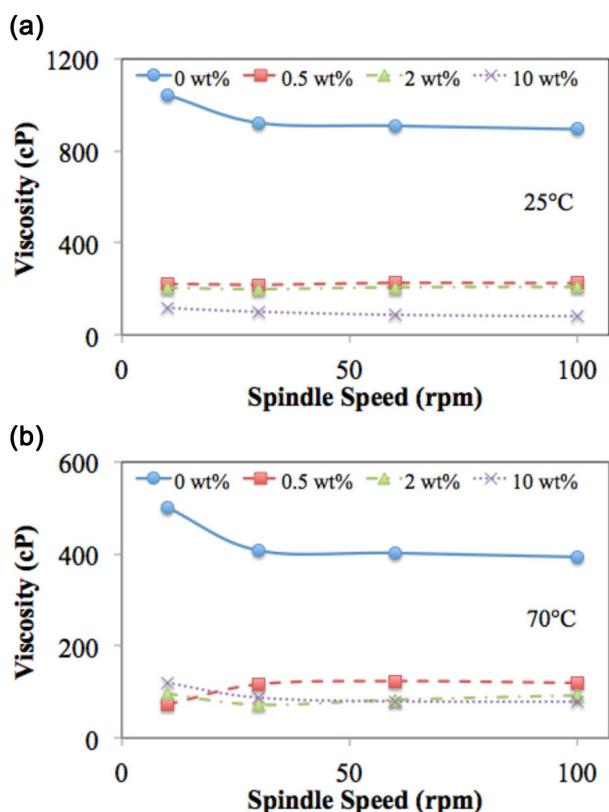


Figure 2. Viscosity measurements of neat PU and PU-Cloisite 30B nanocomposite solutions (0.5, 2, and 10wt%) at (a) 25°C and (b) 70°.

with lower molecular weight are less effective at thickening the solution, higher quantities of clay result in significantly reduced viscosities.

At 25°C, we observed slight shear thinning behavior in the neat PU at low spindle speeds. Conversely, Newtonian behavior was observed for all nanocomposite solutions. Under the higher temperature of 70°C, shear thinning becomes more prominent in neat PU and is also observed in the 2 and 10wt% nanocomposite solutions. Shear thinning behavior is ideal for coating applications as it allows good spreadability and reduces the risk of aggregate formation during processing. In the 0.5wt% nanocomposite solution, slight shear thickening behavior was observed initially at 70°C due to the better dispersion of clay layers at lower loading. At increased spindle speeds, however, the viscosity plateaued, possibly due to the alignment of clay platelets. These observations show that the viscosity of clay-based systems is dependent on the orientation of the platelets.

In summary, we have studied the rheological properties of PU modified with varying clay concentrations. We found the addition of clay to improve the processability of the nanocomposites, leading to a reduction of the overall viscosity. In future work, we intend to examine the morphology of these materials using various analytical techniques and, subsequently, to study their barrier properties.

Author Information

Shirley Peng and Jude Iroh
University of Cincinnati
Cincinnati, OH

References

1. J. M. Herrera-Alonso, E. Marand, J. C. Little, and S. S. Cox, *Transport properties in polyurethane/clay nanocomposites as barrier materials: effect of processing conditions*, **J. Membr. Sci.** **337** (1–2), pp. 208–214, 2009. doi:10.1016/j.memsci.2009.03.045
2. S. W. Guan, *100% solids polyurethane coatings technology for corrosion protection in water and wastewater systems*, **9th Middle East Corros. Conf.**, 2001.
3. M. Joulazadeh and A. H. Navarchian, *Study on elastic modulus of crosslinked polyurethane/organoclay nanocomposites*, **Polym. Adv. Technol.** **22** (12), pp. 2022–2031, 2011. doi:10.1002/pat.1713
4. Z. Wang and T. J. Pinnavaia, *Nanolayer reinforcement of elastomeric polyurethane*, **Chem. Mater.** **10** (12), pp. 3769–3771, 1998. doi:10.1021/cm980448n
5. A. Dorigato, A. Pegoretti, and A. Penati, *Effect of the polymer-filler interaction on the thermo-mechanical response of polyurethane-clay nanocomposites from blocked prepolymer*, **J. Reinf. Plast. Compos.** **30** (4), pp. 325–335, 2011. doi:10.1177/0731684410396599
6. S. Peng and J. Iroh, *Properties of crosslinked polyurethane-clay nanocomposites*, **Proc. SPE ANTEC**, 2015.