

Entangling additives enhance polypropylene foam quality

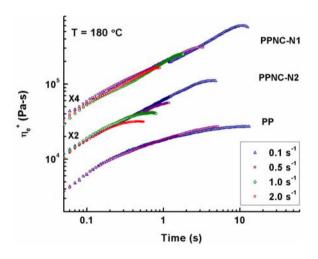
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Combining clay and compatibilizer additives with linear polypropylene forms nanocomposites with a densely entangled inner structure able to produce quality foams upon extrusion.

Linear polypropylene (PP)—composed of long polymer chains devoid of branches or crosslinked structure—and blends of PP with olefinic elastomers are widely used in the automotive and packaging industries. What makes foams produced with these materials of growing interest is their potential to replace the prevalent thermoset polyurethane foams which are not recyclable. However, the production of closed-cell foams with linear PP is difficult because the melt does not exhibit strain hardening under extensional flow.^{1,2} This is problematic as it leads to thinner cell walls during bubble expansion in the foaming process, coalescence of bubbles, and the formation of open-cell foams.^{3,4}

Previous attempts to improve foam quality by adding 5wt% organoclay in amorphous polystyrene have reportedly achieved a 50% reduction in the average cell size⁵. However, the addition of 2 to 3 wt% organoclay to linear PP—with some maleic anhydride grafted PP as a dispersion aid—has only produced a slight improvement in the cellular structure of the foam samples.^{6,7} The PP-clay nanocomposites (NCs) in these previous studies did not display strain hardening in extensional flows. Strain hardening is a requirement for producing closed-cell PP foams with a fully formed cell structure.^{1,2} We, therefore, focused on identifying a suitable combination of additives to produce strain-hardening properties in linear PP.

We prepared several PP-clay NCs from linear PP including different grades of maleic anhydride grafted PP—also known as compatibilizer— with varying molecular weights and maleic anhydride content.^{8,9} We then tested them for strain hardening in extensional flow—defined as the lift of the extensional viscosity at finite strain rates from the base envelope obtained at very low strain rate. Measurements of uniaxial extensional viscosity transients, at 180°C, are presented in Figure 1 for linear PP and five NCs. We observed that the linear PP and the NC melts labeled N2 and N1 did not show any lift while the NC melts labeled S1, S2, and S6 exhibited strain-hardening properties. The weight average molecular weights of the compatibilizers in N2 and N1 were 22,000 and 180,000 respectively; the ratio of maleic anhydride to organoclay was 0.8 g-mol/kg in N2 and only 0.15 g-mol/kg in N1. The



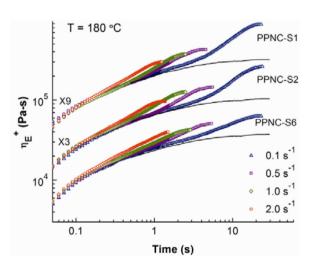


Figure 1. Uniaxial extensional viscosity transients (η_E) at several strain rates for (a) linear PP and nanocomposite (NC) melts labeled N2, N1 and (b) melts labeled S1, S2, S6.

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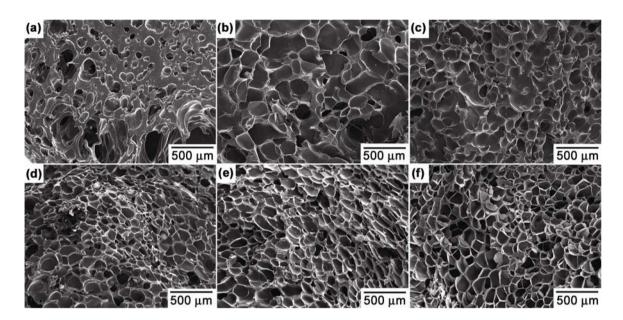


Figure 2. Scanning electron micrographs of extruded foam samples for (a) linear PP foam, (b) PPNC-N2 foam, (c) PPNC-N1 foam, (d) PPNC-S1 foam, (e) PPNC-S2 foam and (f) PPNC-S6 foam.

weight average molecular weight of the compatibilizer was 180,000 in all three strain-hardening NCs; the loading of organoclay was 7 wt% in S1 and S2 and 3 wt% in S6; and the ratio of maleic anhydride to organoclay ranged from 0.2 to 0.3 g-mol/ kg. These results, along with many other test results, revealed that strain hardening during melt extension could be obtained with as little as 3 wt% organoclay if the molecular weight of the compatibilizer was around 180,000 or more and the ratio of maleic anhydride to organoclay was above 0.2 g-mol/kg.

These results suggest that the strain hardening observed in the above experiments stems from the way additives interact at the molecular level. We note that strain hardening observed in the NC melts is analogous to that reported for blends containing small amounts of crosslinked polymer. These blends contain trapped entanglements that reportedly respond to stretching differently than the entanglements on chain segments in the bulk polymer. We believe that linkages or interactions between the clay surface (or its edge) and the maleated polymers of the compatibilizer can form a network of physical crosslinks (or anchor points) between which entanglements may be trapped to produce a similar effect to that observed in blends with crosslinked polymer. In addition, the molecular weight of the compatibilizer needs to be high enough to form a sufficient number of trapped entanglements along the compatibilizer chain between clay surfaces or its edges.

In order to assess the quality of the foam cellular structure in various samples, we then took scanning electron micrographs of extruded foam samples prepared with a fixed level of chemical blowing agent, as shown in Figure 2 ^{9,11–13}. The foam obtained with linear PP alone displayed open cells with very large cell sizes. The mean cell size was

reduced progressively as we moved from PPNC-N2 foam to PPNC-N1 foam and then to the other three NC foams which displayed a higher foam quality in the presence of strain hardening. Both the cell structures and the strain hardening ratios in S1, S2, and S6 were all comparable. We also observed that by treating the organoclay with a silane coupling agent 13—bonding organic and inorganic materials—we obtained an even finer cell structure.

Our work demonstrates that the quality of clay-PP NCs foam structure can be improved by carefully combining additives in order to create a more entangled structure at the molecular level. Future work will focus on developing a better understanding of the entanglement network produced in these systems.

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Continued on next page



10.1002/spepro.003799 Page 3/3

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References

- C. Gabriel and H. Munstedt, Strain hardening of various polyolefins in uniaxial elongational flow, J. Rheol. 47, p. 619, 2003.
- J. Stange and H. Munstedt, Rheological properties and foaming behavior of polypropylenes with different molecular structures, J. Rheol. 50, p. 907, 2006.
- C. H. Lee, K. J. Lee, H. G. Jeong, and S. W. Kim, Growth of gas bubbles in the foam extrusion process, Adv. Polym. Technol. 19, p. 97, 2000.
- 4. C. B. Park and L. K. Cheung, A study of cell nucleation in the extrusion of polypropylene foams, Polym. Eng. Sci. 37, p. 1, 1997.
- C. C. Zeng, X. M. Han, L. J. Lee, K. W. Koelling, and D. L. Tomasko, Polymer-clay nanocomposite foams prepared using carbon dioxide, Adv. Mater. 15, p. 1743, 2003.
- M. F. Champagne and R. Gendron, Structural PP Nanocomposites foams prepared by direct CO2 injection, Soc. Plast. Eng. Tech. Papers 63, p. 1477, 2005.
- M. Guo, M. Heuzey, and P. J. Carreau, Cell structure and dynamic properties of injection molded polypropylene foams, Polym. Eng. Sci. 47, p. 1070, 2007.
- 8. T. Pathak and K. Jayaraman, Polymer clay nanocomposites with improved melt strength, Soc. Plast. Eng. Tech. Papers 65, p. 133, 2007.
- A. K. Chaudhary and K. Jayaraman, Extrusion of linear polypropylene-clay nanocomposite foams tech. rep., 2011.
- M. Yamaguchi, Rheological properties of linear and crosslinked polymer blends: relation between crosslink density and enhancement of elongational viscosity, J. Polym. Sci., Part B: Polym. Phys. 39, p. 228, 2001.
- A. K. Chaudhary and K. Jayaraman, Foaming polypropylene with nanoclays, Soc. Plast. Eng. Tech. Papers, p. 66, 2008.
- A. K. Chaudhary and K. Jayaraman, Extrusion foaming of polymer nanocomposites with distinct strain hardening characteristics, Soc. Plast. Eng. Tech. Papers, p. 68, 2010.
- K. Jayaraman, T. J. Pathak, and A.K. Chaudhary, Novel nanocomposites and nanocomposite foams and methods and products related to same, 2010. US Patent Application No.12/780461