A NEW METHOD TO MODIFY PP FOR IMPROVED MELT STRENGTH

Anthony Marozsan, Philippe Lodefier, Brett Robb, Virginie Chabrol

Total Cray Valley

ABSTRACT

Total Cray Valley (TCV) has developed a new technology to enable producers and compounders to improve the melt strength of conventional PP. Analytical tools show that the addition of inomeric zinc salts into PP at low loading levels induces behavior similar to long chain branched high melt strength PP (HMS-PP). Foam extrusion testing shows that conventional PP produced can be successfully foamed.

INTRODUCTION

Polypropylene (PP) has long been heralded as an important material within the industrial world. PP is a cost-effective, simple-to-process polyolefin with decent chemical stability and myriad properties. One long-standing deficiency, however, is poor melt strength. There are only a few grades of PP available globally with high melt strength known as High Melt Strength PP (HMS-PP).

The traditional approach to improve melt strength has been the chemical addition of high levels of long chain branching to the polymer backbone. Other strategies have proven efficient but introduce into the polymer large amounts of low molecular weight byproducts. Dymalink® 9200 is a zinc salt widely used in the rubber chemical industry. It reacts with aliphatic polymers and corms a C-C link. Within the polymer the zinc salts, thanks to their polar nature, tend to assemble themselves into ionic clusters promoting the formation of a dynamic network. This leads to unusual melt strength behavior even at very low loadings. The following data highlight the use of this mechanism in PP.

MECHANISM

The general mechanism for ionomeric zinc salts has been demonstrated in the literature by Li et al. [1] Through conventional grafting techniques they abducted maleic anhydride groups to PP and then added zinc to open the anhydride groups and create an ionomeric network.

The ionomeric cross links in this study come from the addition of zinc salts without any peroxide. These cross links are formed with reactive zinc acrylates through reactive extrusion with moderate shear at >200 ℃.

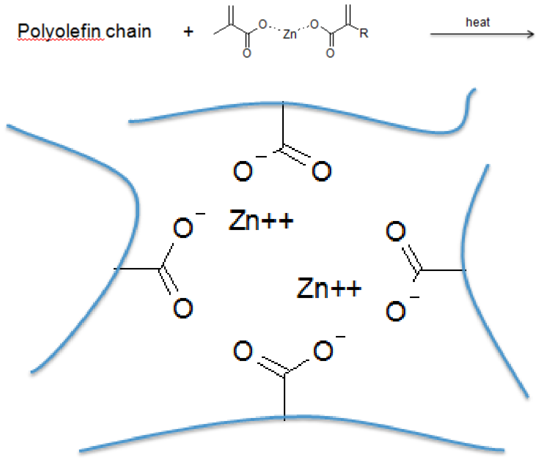

Figure 1. Reaction of zinc salts with polyolefin chain.

The polar zinc salt groups cluster away from the polyolefin chains forming ionomeric domains within the polymer matrix. These domains form as reversible 'crosslinks' with the ionic bonds disassociating at 150 ℃150C. With low loading levels of these additives and conventional twin screw compounding equipment and processes ionomeric behavior is introduced to polypropylene.

In this study a conventional 3.5 melt index homopolymer PP was compounded on a twin screw extruder with 2500ppm of an antioxidant blend, 500ppm calcium stearate, and 0.5 to 2% Dymalink® 9200 zinc diacrylate.

RESULTS

Melt elongation and rheology were studied using a Rheotens 71.97 Gottfert instrument with a 2mm die with an L/D of 15. With the addition of even 0.5% of Dymalink a significant melt elongation effect was observed with the elongation speed for the melt strand increasing from ~250 to ~500 mm/s.

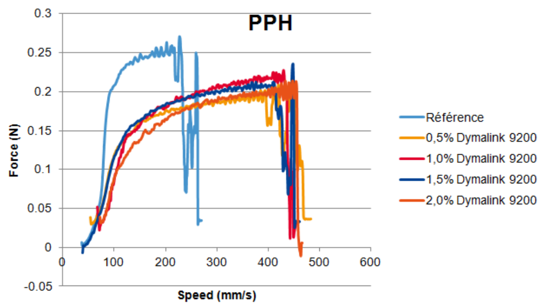

Figure 2. Melt elongation of PPH with and without the addition of Dymalink® 9200

With reactive extrusion one concern is the potential for chain scission of the PP. This is of particular concern with maleinated or peroxide treated PP which typically exhibits an increased low molecular weight fraction. The effect of the reactive extrusion of zinc diacrylate was studied via GPC with the results shown in Figure 3. The molecular weight of the samples was quite constant with the addition of Dymalink and only a small reduction in Mn was observed. The expected cross linking behavior was not observed in the Mz measurement which may be related to the polar solvent used in the GPC method.

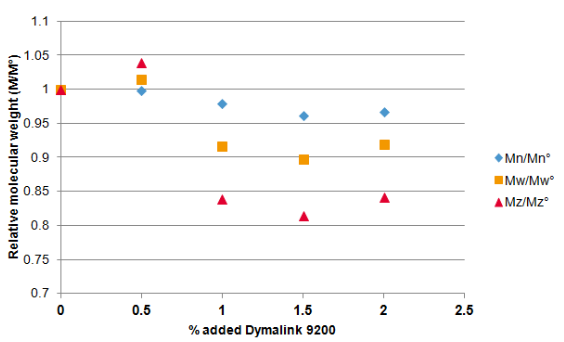

Figure 3. GPC analysis of molecular weight changes in PP with and without Dymalink

One final concern with the addition of salts in PP is the potential nucleating effect of these materials. DSC analysis of the resin with Dymalink added shows no change in melting enthalpy and a small increase of crystallization temperature on cooling for the resin, indicating a slight nucleating effect with Dymalink.

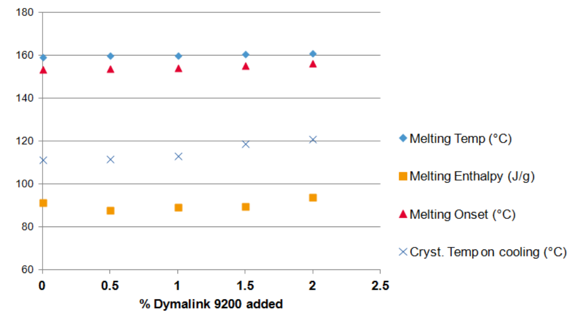

Figure 4. Melting enthalpy effects

A foaming trial was also carried out with 3.5 melt index homopolymer PP, 0.5% talc, and 1% Dymalink 9200. Materials were processed on a single screw extruder at 240°C with a static mixer feeding CO_2 liquid at 74bar. Compared to unmodified resin the extruded material with Dymalink exhibited a smooth surface appearance with better foam morphology indicating successful foaming. Figured 5 and 6 show SEM images of the material with and without Dymalink respectively. Without the improved melt strength imparted by Dymalink the conventional resin has poor cell morphology with open cell content, irregular sizes, and poor surface morphology. With Dymalink the cell structure is homogenous with good closed cell content.

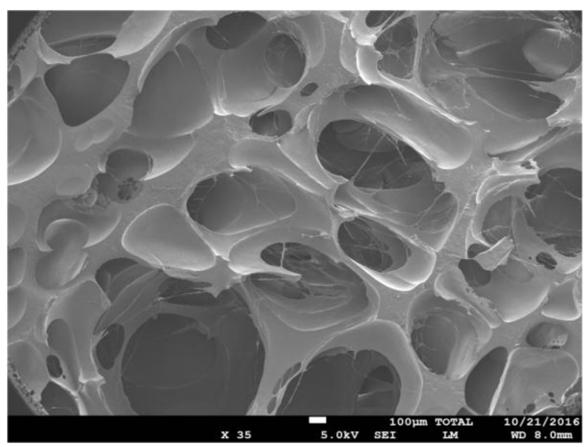

Figure 5. SEM image of conventional PP processed with 0.6mL/min CO_2 at 130 bar die pressure

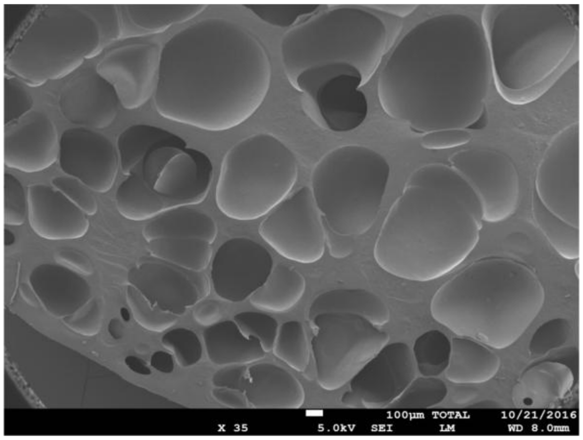

Figure 6. SEM image of conventional PP modified with 1% Dymalink® 9200 processed with 0.6mL/min CO_2 at 130 bar die pressure

MATERIAL AVAILABILITY

Dymalink® 9200 and Dymalink® 9201 are TSCA and REACH registered with global availability. Food contact approval is underway.

CONCLUSIONS

Zinc salts represent a new class of polyolefin additives with a novel set of performance attributes. Addition of zinc salts to conventional PP improves the melt strength of the resin with very few observed drawbacks. This allows a greater freedom to tailor compounds to specific end use needs vs. the use of conventional HMS-PP. These materials are now commercially available globally.

References

1. Li et al, Polymers 70 (2015), 207