

Effects of SureFlo[®] on the Crystallization and Melting Behavior of Semi-Crystalline Polyethylene (PE) and Polypropylene (PP) Systems

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SureFlo[®] is a new and cost-effective process additive for general-purpose plastics such as polyethylene (PE), polypropylene (PP), polystyrene (PS), ABS, Nylon and PET. It is a proprietary blend of hydrocarbon resins in an easily handled pellet form that flows at normal plastic processing temperatures. The benefits of SureFlo[®] include

- Enhances the processibility of the material by reducing melt viscosities
- Delays the crystallization of semi-crystalline polymers to facilitate mold flow
- Helps compatibilize dissimilar plastic components and contaminants
- Serves as a cost-effective black colorant

In a previous report,^[1] we have demonstrated the effectiveness of using a small amount of SureFlo to reduce melt viscosities of polyethylene. This can be utilized to lower the processing temperatures for faster cycle time (increased productivity) and reduced energy cost.

Here, we study the effects of adding SureFlo on the crystallization and melting behavior of semi-crystalline polymers such as polyethylene (PE) and polypropylene (PP).

Experimental

Four semi-crystalline polymers were used in this study. They are (1) a polypropylene homopolymer (Polypropylene 3281 from Total Petrochemicals USA, Inc.; quoted melt index = 1.25 g/10 min), (2) a polypropylene copolymer (CP310 from M. Holland Company; quoted melt index = 7.0 g/10 min), (3) an injection-molding grade

HDPE (HD300 from M. Holland Company; quoted melt index = 7.0 g/10 min), and (4) a blow-molding grade HDPE (HD100 from M. Holland Company; quoted melt index = 0.35 g/10 min). They are designated as (1) PP-HP, (2) PP-CP, (3) PE-HM (high melt) and (4) PE-LM (low melt), respectively. Each material was compounded with SureFlo[®] at 5 and 10 wt-% levels.

A TA-Q2000 differential scanning calorimeter (DSC) equipped with a RCS-90 cooling unit (TA Instruments) was used for the study. For each experiment, a small amount of sample (5-10 mg) was first encapsulated in a T_{zero} aluminum pan. The sample was then heated to 220 °C (1st heating), cooled to -20 °C (cooling), and finally heated to 220 °C (2nd heating) while collecting the heat flow data. All heating/cooling rates were 20 °C/min.

Results and Discussion

Fig. 1 shows the cooling and 2nd heating DSC thermograms of all the samples tested. For neat PP-HP, PE-HM and PE-LM, a single melting peak is observed upon heating (2nd row in **Fig. 1**). For PP-CP, in addition to the major melting peak at c.a. 160 °C, a minor peak at c.a. 120 °C is also seen and attributed to the copolymerized polyethylene blocks that are present in the polymer backbones. Unlike many small-molecule additives, adding SureFlo[®] at 5 and 10% does not lead to any reduction of melting temperatures (T_m's). For PP-HP, PE-HM and PE-LM the T_m stays almost unchanged while for PP-CP a slight increase of the second T_m (T_m of PP crystals) is indeed

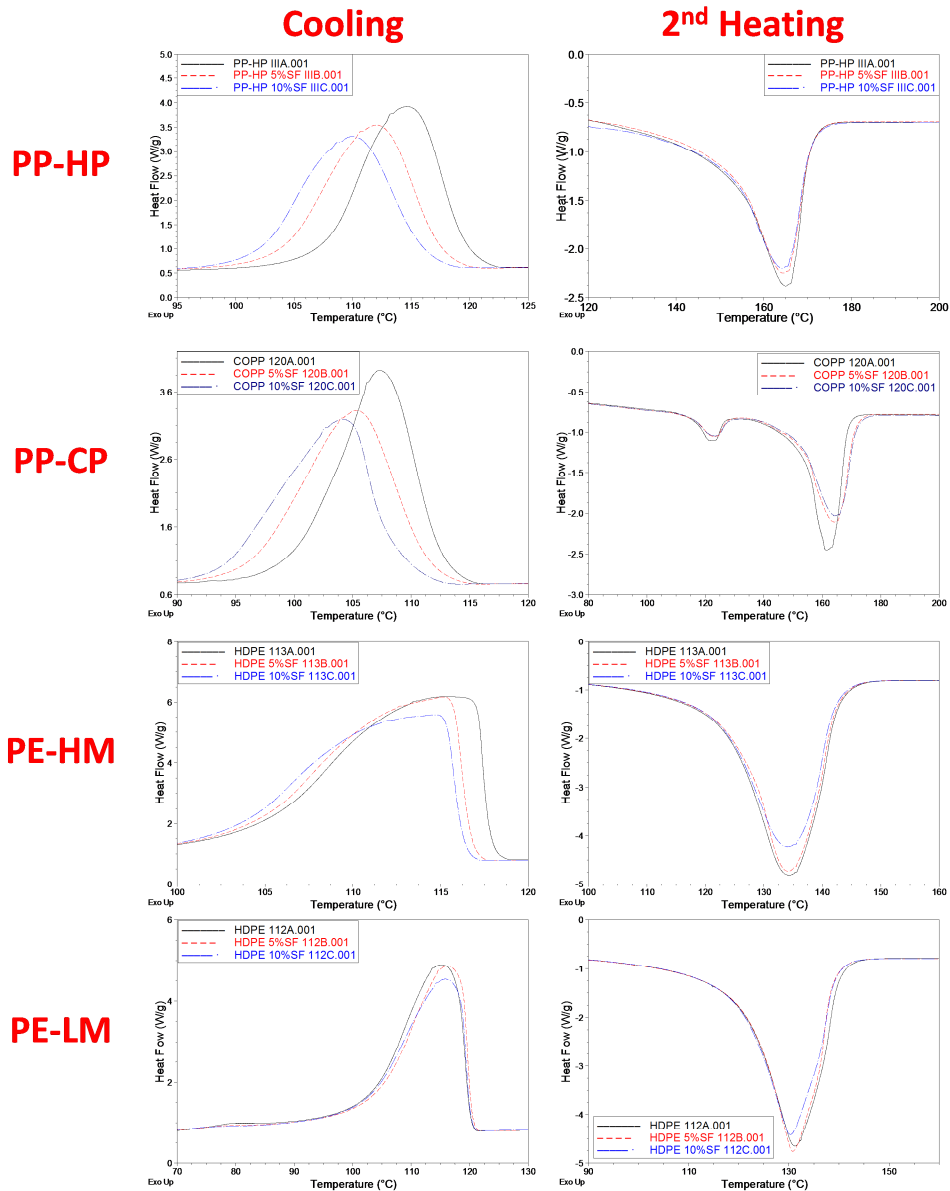


Fig. 1 DSC thermograms of (from left to right) PP-HP, PP-CP, PE-HM and PE-LM. Both the cooling and 2nd heating traces are shown for neat polymer (black), 5% SureFlo[®] (red) and 10% SureFlo[®] (blue).

observed with the addition of SureFlo[®]. Since T_m is related to the average thickness of the lamellar structure, we can conclude that adding SureFlo[®] does little change to the crystal structures of the base polymers.

Unlike 2nd heating, the cooling traces become noticeably different with the addition of Sureflo[®] for PP-HP, PP-CP and PE-HM (1st row of **Fig.1**). More specifically, the

crystallization temperature (T_c) decreases with increasing levels of SureFlo[®] under the same cooling rate of 20 °C/min. This effect is the exact opposite to the heterogeneous nucleation observed for many plastic additives/fillers and means that the crystallization is delayed.

To better understand this, the x-axis was converted to time and the onset of

cooling from 220 °C is defined as “time zero”. The heat flow vs. time profiles for PP-HP, PP-CP and PE-HM are shown in the first column of **Fig. 2**. Clearly, crystallization is delayed with increasing levels of SureFlo[®]. We further calculated the degree of crystallinity (DoC) using the equation:

$$\chi_c(t) = \frac{\int_0^t H(t)dt}{\Delta H_0} \times 100\%$$

where $H(t)$ is the heat flow in W/g at time t and ΔH_0 is the heat of fusion, i.e. the theoretic heat of melting of a 100% crystalline polymer. The literature ΔH_0 values^[2] of 146.5 J/g (for PP) and 295.7 J/g (for PE) were used for calculation and the results are shown in the 2nd column of **Fig. 2**. It can be seen that SureFlo[®] affects mainly the onset of crystallization, or the “induction time”. The crystallization rate (indicated by the slope of the DoC vs. time plot) is less affected.

The exact mechanism of SureFlo on crystallization kinetics is not fully understood. It is possibly due to the reduced viscosities^[1] which affect the chain-folding dynamics. It is also not clear why such an effect is not observed in PE-LM which requires further studies.

In practice, the delayed crystallization allows longer flow time before the melt crystallizes into a solid part. This is beneficial for injection molding applications. During injection molding, cooling and crystallization all take place in the cold mold. Delayed crystallization leads to longer in-mold flow time of the polymer melt to facilitate mold-filling, especially with complex geometries and fine features. This also explains the enhanced

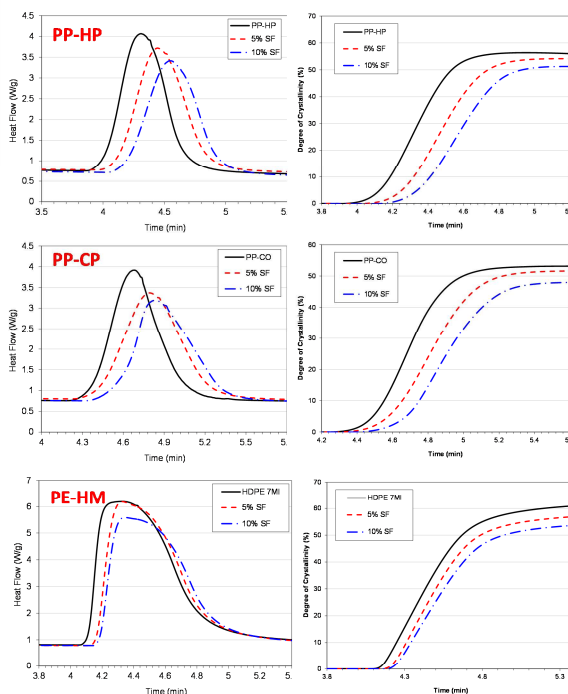


Fig. 2 Converted heat flow vs. time profiles for PP-HP, PP-CP and PE-HM upon cooling (1st column) and the calculated crystallinity vs. time curves.

mold flow and better preserved features that were observed in most plant trials.

Conclusions

In this report, the effects of SureFlo[®] on crystallization and melting behavior of semi-crystalline PE and PP polymers were studied by DSC. It was found that SureFlo[®] does not change the melting temperatures of the base polymers. This ensures good physical properties of finished products. The delayed crystallization is beneficial for injection molding applications to enhance mold-flow and mold-filling.

References

- [1] **Effect of SureFlo[®] on the melt viscosity of polyethylene**, *Flow Polymers Technical Brief*, available upon request.
- [2] *Polymer Data Handbook*, Oxford University Press, Inc., 1999 (electronic version)