Is it possible to increase polypropylene melt strength via UV radiation?

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Polypropylene (PP) is a commodity plastic that can be used for various applications. Conventional methods for synthesizing PP result in low melt strength and low extensional viscosity in the polymer melt. In order to accommodate processing requirements in applications such as film blowing, blow molding, extrusion coating, thermoforming, foaming and fiber spinning, long chain branches should be introduced to the PP structure. The presence of long chain branches results in larger extensional viscosity and melt strength in PP\textsuperscript{1,2}.

For modification with UV radiation, photoinitiators such as benzophenone (BPH) have been used and UV energy is utilized to activate these photoinitiators\textsuperscript{3,4}. In this work, PP is modified in the solid state using BPH as photoinitiator. The operating conditions that maximize strain hardening in PP were identified. Processing conditions such as radiation time, UV lamp intensity and cooling rate, along with the concentration of the photoinitiator, were manipulated to yield maximum amount of long chain branching (LCB) in the PP structure. One issue that arises during modification of polymers by UV radiation is related to the depth of radiation\textsuperscript{5}. It is known that penetration of UV light is limited and this can cause inhomogeneities in LCB (and crosslinking (CL)) of the samples\textsuperscript{6,7}. The effects of radiation duration and sample thickness on the amount of long chain branches were also investigated. Linear viscoelastic (LVE) properties, molecular weight (MW), and gel content were determined and compared for runs having different sample thicknesses, irradiated for different times.

**Experimental Procedures and Characterization**

PP homopolymer (Pro-fax PH 382M) from LyondellBasell with a melt flow rate (MFR) of 3.5 g/10 min was melt-mixed in a batch mixer at 190 °C (100 rpm) with benzophenone (Sigma Aldrich).

The samples were ground using a Wiley mill (model 1102, Arthur H. Thomas Co.). After grinding, PP-initiator blend granules were compression-molded into sheets at 190 °C under an applied force of 4,400 N for five minutes. The sheets were subsequently irradiated using a mercury UV lamp (Versa Cure) with total power of 1.8 kW.

Parallel plate rheometry (AR2000, TA instruments) and GPC measurements (Polymer CHAR, Spain) were used to determine linear viscoelastic properties (LVE) and molecular weight (MW) averages, respectively. ASTM D2765-11 was followed to measure sample gel content. The extensional flow properties of modified samples were measured using the Sentmanat extensional rheometer (SER) universal testing platform (Xpansion instruments).
A constant stress parallel plate rheometer was used to obtain storage modulus ($G'$), loss modulus ($G''$), complex modulus ($G^*$), loss tangent ($\tan \delta$), and complex viscosity ($\eta^*$) at different angular frequencies ($\omega$). Having $\eta^*$ vs. $\omega$, the power-law shear thinning index ($n$), zero shear viscosity ($\eta_0$) and relaxation time ($\lambda$) of the polymer melt were acquired by fitting the Cross model (Equation 1) to the data.

$$\eta^* = \frac{\eta_0}{1 + (\omega \lambda)^n}$$  \hspace{1cm} \text{Equation 1}

It has been observed that long chain branched PP has higher $\eta_0$, $\lambda$ and lower $n$ than the linear parent PP. On the other hand, smaller $\eta_0$, longer Newtonian plateau (smaller $\lambda$) and larger shear power-law index compared to the parent PP can be evidenced in degraded linear PP.

Rheological polydispersity indices were determined using Equation 2 and 3.

$$\text{PI} = 10^5 \frac{G_c}{G_c(Pa)}$$  \hspace{1cm} \text{Equation 2}

$$\text{ER} = C_1 G'_c \text{at } G'' = 500 \text{ Pa}$$  \hspace{1cm} \text{Equation 3}

$G_c$ in Equation 2 is the crossover modulus. In Equation 3, $C_1$ is the slope of the log ($G'$) versus log ($G''$) curve. It should be noted that ER is only sensitive to the distribution of high MW chains. Runs with larger ER values indicate a broader distribution of the higher molecular weight chains. Increasing values of PI indicate broadening of the molecular weight distribution (MWD) in general.

**Results and Discussion**

In order to identify the processing conditions that maximize the LCB level in PP, the process operating conditions (photoinitiator concentration, duration of radiation, UV lamp intensity, cooling air pressure, and combinations thereof) were manipulated within the range summarized in Table 1.

<table>
<thead>
<tr>
<th>Factor</th>
<th>Process variable (units)</th>
<th>Ranges</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Photoinitiator concentration (wt %)</td>
<td>0.1-0.5 (with respect to polymer mixture)</td>
</tr>
<tr>
<td>B</td>
<td>Duration of radiation (s)</td>
<td>120-600</td>
</tr>
<tr>
<td>C</td>
<td>UV lamp intensity (%)</td>
<td>47-100 (with respect to total lamp intensity)</td>
</tr>
<tr>
<td>D</td>
<td>Cooling air pressure (%)</td>
<td>0-100 (with respect to total air flow pressure)</td>
</tr>
</tbody>
</table>

D-optimal design of experiments and statistical analysis were utilized to find the combinations of these variables (within the ranges mentioned in Table 1) that result in the greatest amount of LCB. Shear thinning index ($n$), zero shear viscosity($\eta_0$), relaxation time ($\lambda$), and ER were calculated using $\eta^*$, $G'$ and $G''$ vs. $\omega$ measurements (Equations 1 to
3). A criterion can be set for each of these responses (n, \( \eta_0 \), \( \lambda \) and ER) to identify the processing window that results in long chain branching rather than degradation. Table 2 shows the chosen criteria to find the optimized processing conditions.

Contour plots corresponding to these criteria (Table 2) are shown in Figure 1; the optimal processing window, which satisfies these limits for the response variables (Table 2) is the yellow area. Figure 1 shows that samples with a high concentration of BPH (above 0.2 wt-%) which are radiated for times larger than 4 minutes at low lamp intensity at temperatures below 60 °C yield larger amounts of LCB.

| Table 2: Criteria chosen for each response variable to find optimized processing conditions |
|---|---|
| **Response** | **Criteria** |
| n | <0.57 |
| \( \eta_0 \) (Pa.s) | >90,000 |
| \( \lambda \) (s) | >0.67 s |
| ER | >2.0 |

Figure 1: Conditions that yield high degree of LCB

Two runs in the processing range indicated in Figure 1 were chosen along with the parent PP for extensional rheometry measurements. The processing conditions for these two runs are cited in Table 3.

| Table 3: Experimental conditions of the runs chosen within the optimized region |
|---|---|---|---|
| **Run ID** | **Photoinitiator concentration (wt%)** | **Duration of radiation (s)** | **UV lamp intensity (%)** |
| PP | - | - | - |
| 1 | 0.5 | 600 | 47 |
| 2 | 0.3 | 360 | 74 |

Figure 2 shows the uniaxial tensile stress growth coefficient \( (\eta^+_E) \) of the parent PP and runs 1, 2 at four different Hencky strain rates (0.01, 0.1, 1 and 10 s\(^{-1}\)). The dashed lines in Figure 2 represent three times the shear stress growth coefficient (i.e., \( 3\eta^+_0(t) \)). The parent PP shows a slight increase in uniaxial tensile stress growth, which might be due to
the presence of high MW linear chains and the broad MWD of the parent PP. $\eta_{+}^E$ clearly increased at all strain rates for runs 1 and 2 (compared to the parent PP). This provides clear and convincing evidence of a larger melt strength in runs 1 and 2, which have been modified under the conditions of Figure 1.

![Figure 2: Uniaxial tensile stress growth coefficient ($\eta_{+}^E$) at Hencky strain rates of 0.01, 0.1, 1 and 10 s$^{-1}$](image)

Figure 2: Uniaxial tensile stress growth coefficient ($\eta_{+}^E$) at Hencky strain rates of 0.01, 0.1, 1 and 10 s$^{-1}$

The next goal of this work was to study the effects of UV penetration depth along with UV radiation duration on the amount of LCB in the modified samples. For this purpose, solid discs (PP mixed with 0.5 wt-% BPH) with different thicknesses were radiated for different lengths of time at the same processing window of Figure 1 (47 % lamp intensity). Three-level factorial design experiments were conducted (Table 4). In Table 4, run 10 is PP after melt mixing with BPH and run 11 is the parent PP.

Table 4: Design of experiments for 3-level factorial design

<table>
<thead>
<tr>
<th>Run ID</th>
<th>BPH (wt-%)</th>
<th>Thickness-A (mm)</th>
<th>Time-B (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.5</td>
<td>1</td>
<td>5</td>
</tr>
<tr>
<td>2</td>
<td>0.5</td>
<td>1</td>
<td>10</td>
</tr>
<tr>
<td>3</td>
<td>0.5</td>
<td>1</td>
<td>15</td>
</tr>
<tr>
<td>4</td>
<td>0.5</td>
<td>2</td>
<td>5</td>
</tr>
<tr>
<td>5</td>
<td>0.5</td>
<td>2</td>
<td>10</td>
</tr>
<tr>
<td>6</td>
<td>0.5</td>
<td>2</td>
<td>15</td>
</tr>
<tr>
<td>7</td>
<td>0.5</td>
<td>3</td>
<td>5</td>
</tr>
<tr>
<td>8</td>
<td>0.5</td>
<td>3</td>
<td>10</td>
</tr>
<tr>
<td>9</td>
<td>0.5</td>
<td>3</td>
<td>15</td>
</tr>
<tr>
<td>10</td>
<td>0.5</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>11</td>
<td>0</td>
<td>1</td>
<td>0</td>
</tr>
</tbody>
</table>

Values for $\eta_0$, $\lambda$, n and polydispersity indices (PI and ER) of the runs are summarized in Table 5. It can be seen that all radiated runs (1 to 9) have larger $\eta_0$, $\lambda$, PI and ER, and lower n values compared to run 10, which is PP after melt mixing with BPH. Comparison between runs 1, 2 and 3 shows that longer exposure time to UV results in larger $\eta_0$, $\lambda$, PI and lower n values (Table 5). This trend is also observed for the 2 mm (runs...
4, 5 and 6) and 3 mm (runs 7, 8, and 9) samples. On the other hand, an increase in the thickness of the samples limits UV light penetration and subsequently results in lower $\eta_0$, $\lambda$ and higher $n$ at the same exposure times (compare runs 1, 4 and 7, or 2, 5 and 8, or 3, 6 and 9). This is because all these LVE constants are indicators of an average property within the sample. Therefore, due to the limited UV penetration in the samples, formation of LCB or CL is not uniform in thicker samples.

In order to investigate the presence of gel (due to crosslinking) in each run, results from extraction experiments are also summarized in Table 5. Increases in radiation time cause larger percentage of CL (gel) in the samples with the same thickness. Moreover, a decrease in thickness increases the percentage of gel in the runs. An increase in gel content upon increasing radiation time is more significant at low thicknesses. This is the same trend observed in rheological properties earlier.

Table 5: Viscoelastic properties, molecular weight and gel content of the runs

<table>
<thead>
<tr>
<th>Run ID</th>
<th>$\eta_0$ (kPa.s)</th>
<th>$\lambda$ (s)</th>
<th>n</th>
<th>PI</th>
<th>ER</th>
<th>Gel (%)</th>
<th>$M_n$ (kg/mol)</th>
<th>$M_w$ (kg/mol)</th>
<th>$M_z$ (kg/mol)</th>
<th>PDI</th>
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<tr>
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<td>2</td>
<td>16.7</td>
<td>12.3</td>
<td>0.47</td>
<td>4.78</td>
<td>1.95</td>
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<td>259.1</td>
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<td>3</td>
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<td>0.96</td>
<td>0.51</td>
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<td>71.8</td>
<td>329.6</td>
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<td>5</td>
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<td>67.5</td>
<td>357.3</td>
<td>919.3</td>
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<td>7</td>
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<td>0.55</td>
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<tr>
<td>9</td>
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<td>1.39</td>
<td>1.6</td>
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<td>317.9</td>
<td>591.2</td>
<td>4.2</td>
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<tr>
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<td>9.3</td>
<td>0.79</td>
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<td>-0</td>
<td>78.4</td>
<td>361.4</td>
<td>714.8</td>
<td>4.6</td>
</tr>
</tbody>
</table>

These results have recently been extended to include the effect of acrylic co-agent on PP modification, and these more recent results will be discussed during the IPR poster session (in a related poster).

References

Is It Possible to Increase Polypropylene Melt Strength via UV Radiation?

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Overview

Why? • Why is melt strength important? • Why UV radiation?

How? • How to increase PP melt strength? • How to optimize the procedure?

What? • What are the limitations? • What are the solutions?

Why is melt strength important for PP?

✦ Melt strength: polymer resistance to extensional deformation

- Entanglements
- Chain interactions

Why UV radiation?

Peroxides
- Toxic
- Controlling the process

e-beam and gamma
- Cost
- Availability
- Safety

Synthesis
- Requires new plants

UV radiation
- Safe
- Available
- Easy to control
- Affordable

Why UV?

How UV irradiation can be used for PP modification (mechanism)

Photoinitiator

UV irradiation

Hydrogen abstraction

How UV irradiation can be used for PP modification (mechanism)

- β-scission
- Disproportionation Degradation
- Chain combination
- Long chain branching

Linear polymer
- Short chains & narrow molecular weight distribution
How to modify PP via UV irradiation (process steps)

- Mixing PP with photoinitiator (PI)
- Irradiation with UV lamp
- Grind
- Hot press

What are the processing factors/variables?

- Processing variables and ranges
- Design of experiments
  - D-optimal; Design Expert was used; 32 experimental runs
- Responses
  - Viscoelastic properties ($\eta_0, \lambda$ and $n$)
  - Rheological polydispersity indices (PI and ER)

Extensional viscosity

- The viscosity of a polymer melt under extensional stress
- Evaluation of extensional (elongational) viscosity
- Extensional rheometers: Sentmanat extensional rheometer

PP shows strain hardening

Possible limitations?

- Radiation depth (UV penetration limit?)
- Radiation time

Study the effect of radiation time and depth

<table>
<thead>
<tr>
<th>Variable (units)</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample thickness (mm)</td>
<td>1-3</td>
</tr>
<tr>
<td>Duration of radiation (min)</td>
<td>5-15</td>
</tr>
<tr>
<td>BPH Concentration (wt-%)</td>
<td>0.5</td>
</tr>
<tr>
<td>UV lamp intensity (%)</td>
<td>47</td>
</tr>
<tr>
<td>Cooling air pressure (%) Temperature</td>
<td>100(&lt;50 °C)</td>
</tr>
</tbody>
</table>
The effect of thickness on complex viscosity

![Graph showing the effect of thickness on complex viscosity]

Further reduction of radiation duration: Co-agent

- What are co-agents?
- What is the mechanism?
- What are the challenges?

Study of the effect of co-agent on long chain branching and gel content

- Objective
  - Min gel; Max branching content
- Central composite design of experiments

<table>
<thead>
<tr>
<th>Variable (units)</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co-agent conc. (wt-%)</td>
<td>0.25-0.75</td>
</tr>
<tr>
<td>BPH conc. (wt-%)</td>
<td>0.1-0.5</td>
</tr>
<tr>
<td>Radiation duration (s)</td>
<td>4-65</td>
</tr>
<tr>
<td>UV lamp intensity (%)</td>
<td>47</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>&lt;50</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Response</th>
<th>Specs</th>
</tr>
</thead>
<tbody>
<tr>
<td>n</td>
<td>&lt;0.49</td>
</tr>
<tr>
<td>η* (kPa.s)</td>
<td>&gt;50</td>
</tr>
<tr>
<td>λ (s)</td>
<td>&gt;50</td>
</tr>
<tr>
<td>ER</td>
<td>&gt;1.3</td>
</tr>
<tr>
<td>Gel content (%)</td>
<td>&lt;5</td>
</tr>
</tbody>
</table>

Example of operating map

Formation of LCB under these conditions is confirmed via GPC

- Low co-agent concentration
- High BPH concentration

Concluding Remarks

- UV radiation is a safe, nontoxic method for PP modification
- UV radiation can be used to produce long chain branched PP (larger melt strength for packaging, thermoforming, blow-molding, extrusion coating and foaming applications)
- Variables such as photoinitiator type and concentration, lamp intensity, radiation time and temperature affect the process
- UV penetration depth and radiation time are possible limitations of the UV modification process
- Addition of co-agent decreases the radiation time needed for formation of long chain branching significantly
- US patent application for this work
References

2. Figure copied from: http://pubs.rsc.org/en/content/articlehtml/2013/sm/c2sm27233d
9. Figure copied from: http://www.competitiveextrusion.org/technology/controls/PIR-Characteristics-of-branched-polymers-used-for-extrusion.html
10. Figure copied from: http://www.competitiveextrusion.org/technology/controls/PIR.html

How to characterize long chain branching (LCB) vs. degradation

Reference for comparisons: Linear PP with broad molecular weight distribution (MWD)

<table>
<thead>
<tr>
<th>Rheological properties</th>
<th>Degradation</th>
<th>LCB</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>G' at low frequencies</td>
<td>Higher G'</td>
<td></td>
<td>more elastic</td>
</tr>
<tr>
<td>G'' slope at low frequency</td>
<td>Indication of LCB</td>
<td></td>
<td></td>
</tr>
<tr>
<td>n' at low frequencies</td>
<td>n' = k molecular weight</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Relaxation time (λ)</td>
<td>Shorter plateau region for LCB</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rheological polydispersity indices</td>
<td>Pi and ER</td>
<td></td>
<td>broader molecular weight distribution</td>
</tr>
</tbody>
</table>

G': Storage modulus   G'': Loss modulus     tan δ: Loss angle   η*: Complex viscosity
Pi: Rheological polydispersity index   ER: Dispersity of high molecular weight tail of MWD

The effect of modification on η* ~ ω

Runs 1 and 2 have larger n, λ and more shear thinning behavior (n) compared to the parent PP
The effect of modification on tan δ vs. G* (related to molecular weight distribution)

Higher energy storage in longer chains at low frequencies

In runs 1 and 2, slope is smaller

The effect of modification on G’-ω

Long chain branched

Higher energy storage in longer chains at low frequencies

In runs 1 and 2, slope is smaller

Examples of operating maps

Low temperature
High BPH Concentration

Long radiation time
Low lamp intensity

DEBPH does not show conclusive evidence for LCB

How to introduce long chain branching (LCB) to PP?

Why?

Determining molecular weight distributions

Runs 1 and 2 have a tail at high molecular weights
Run 3 is shifted towards low molecular weights
The effect of modification on intrinsic viscosity \( [\eta] \)

- Long chain branched PP has lower \( R_g \) compared to linear PP

\[
[\eta] \propto \frac{R_g}{M}
\]

The effect of thickness on storage modulus

- Increase in thickness
  - 1 mm-15 min
  - 2 mm-15 min
  - 3 mm-15 min
  - Parent PP

The effect of sample thickness on the relaxation spectrum

- \( G'(\omega, \lambda) = \int_0^\infty H(\lambda) \cdot \left(\frac{\omega}{\omega + (\gamma/\lambda)^2}ight) d\omega \)

- \( G''(\omega, \lambda) = \int_0^\infty H(\lambda) \cdot \left(\frac{\omega}{\omega + (\gamma/\lambda)^2}ight) d\omega \)

- \( H(\lambda) \) is the relaxation function
  - 1 mm-15 min
  - 2 mm-15 min
  - 3 mm-15 min
  - Parent PP

The effect of radiation time on storage modulus

- Increase in radiation time
  - 1 mm-5 min
  - 1 mm-10 min
  - 1 mm-15 min
  - Parent PP