Correlation of Test Methods to evaluate the Thermal Stability of neat PVC Resin

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Alex Wegmann; Shandy Li
Ciba R&D Center, Plastic Additives, Shanghai, China
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• Evaluating thermal stability of PVC by different methods
  – Evaluation of neat PVC resins
  – Evaluation of PVC compounds
  – Correlation between different methods
PVC industry
S-PVC Polymerization Process

- **Chain stoppers** terminate the polymerization and quench catalyst residues, thereby avoiding further polymerization reactions that can lead to polymer deposits in strippers and dryers.

- Some sterically hindered phenols also demonstrate a quite good efficiency as chain stoppers; in addition, they are also very effective **antioxidants**, protecting PVC under thermo-oxidative conditions.
### Structure of chain stoppers / antioxidants

<table>
<thead>
<tr>
<th>Acetone-thio-semi-carbazone (ATSC)</th>
<th>Bisphenol A (BPA)</th>
<th>Ciba® IRGANOX® 1076</th>
</tr>
</thead>
<tbody>
<tr>
<td>CGX AO 145 (80%)</td>
<td>IRGANOX® 1076 (20%)</td>
<td>Ciba® IRGANOX® 245</td>
</tr>
</tbody>
</table>

= Ciba® IRGASTAB® PVC 11
Evaluating chain stopping performance

Pressure drop during PVC polymerization:

**Chain terminator** is added at 70% conversion rate to check its efficiency in the lab process

- **No chain-stopper:** VCM consumption causes pressure drop
- **Ideal chain-stopper:** Terminates polymerization completely (no pressure drop)
- „**Non-ideal“ chain-stopper:** Pressure drop only reduced (not 100% effective)
Efficiency of different chain stoppers

- Hindered phenols can be almost as good as ATSC in chain terminating.
- The degree of sterical hindrance of the phenol group seems to determine the efficiency in chain stopping:
  - Full sterical hindrance (2 tert-butyl groups), like in Ciba® IRGANOX® 1076, shows a very low chain stopping efficiency.
  - Less hindered molecules, like IRGANOX® 245 (1 tert-butyl, 1 methyl group) and CGX AO 145 (1 methyl, 1 secondary alkyl group) are better in chain terminating.
Thermal degradation of PVC

- **Dehydrochlorination (DHC):**

  ![Dehydrochlorination reaction]

  - DHC and autoxidation proceed simultaneously and influence each other
  - HCl (autocatalytic) and O₂ (defects formed by autoxidation) catalyze DHC
  - DHC is reduced during processing by adding heat stabilizers (metal soap)
  - Autoxidation is reduced by antioxidants during production and processing

- **Autoxidation:**

  ![Autoxidation reaction]
Discoloration occurs during degradation

A direct consequence of the dehydrochlorination ("unzipping"), also involving oxidation and chain-scission reactions, is discoloration of PVC.
Evaluation of thermal degradation of PVC

• Evaluation of neat PVC resin
  (without any heat stabilizer or other components added):
    – Dehydrochlorination (DHC)
    – Discoloration after compression molding
    – Static oven aging of PVC powder (discoloration)

• Evaluation of PVC compounds
  (formulated with heat stabilizers and possibly other components)
    – Discoloration after processing on a 2-roll-mill (dynamic heat stability)
    – Discoloration of PVC sheets in a gradient oven (static heat stability)
    – Measuring the molecular weight decrease due to chain-scission of PVC with a torque rheometer
Evaluation of neat PVC resin

Dehydrochlorination

Compression molding
Evaluation of dehydrochlorination (DHC)

On heating, PVC releases HCl, that increases the conductivity or pH of an aqueous solution in which HCl is trapped.
### Dehydrochlorination (DHC) performance

<table>
<thead>
<tr>
<th>Concentration/Compound</th>
<th>Time (minutes) to Reach a Conductivity of 200 micro Siemens/cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>150ppm IRGANOX 245</td>
<td>60</td>
</tr>
<tr>
<td>150ppm IRGASTAB PVC 11</td>
<td>60</td>
</tr>
<tr>
<td>50ppm ATSC + 100ppm BPA</td>
<td>50</td>
</tr>
<tr>
<td>50ppm ATSC + 100ppm IRGANOX 1076</td>
<td>50</td>
</tr>
<tr>
<td>150ppm IRGANOX 1076</td>
<td>45</td>
</tr>
<tr>
<td>50ppm ATSC</td>
<td>40</td>
</tr>
</tbody>
</table>

- Sterically hindered phenols can increase the stability of PVC resin. Especially, **partially hindered phenols** are very effective, e.g. IRGASTAB® PVC 11, IRGANOX® 245.
- **Fully hindered phenols**, like IRGANOX® 1076, or completely **unhindered phenols**, like Bisphenol A (BPA), show lower efficiency.
- IRGANOX® 1076 shows lower DHC performance than IRGANOX® 1076 + ATSC, because part of the IRGANOX® 1076 is used up for chain stopping.
- Pure **Chain stoppers**, like ATSC, show low performance in DHC test.
Discoloration during compression molding

- The lower the yellowness index (YI), the higher the lightness (L*) of PVC plaques made from neat PVC resin, and thus the better the thermal stability.
- Sterically hindered phenols can effectively reduce the discoloration of PVC resin at high temperature.
Evaluation of PVC compounds
Discoloration after 2-roll-mill processing

PVC sheets containing sterically hindered phenols have better color retention compared to PVC sheets with only chain stoppers.
Correlation between DHC and molding

Yellowness index / lightness*1.5

- Yellowness index
- Lightness*1.5
- DHC stability

- 50ppm ATSC
- 50ppm IRGANOX 1076
- 50ppm ATSC+100ppm BPA
- 150ppm IRGANOX 1076
- 50ppm IRGASTAB PVC 11
- 150ppm IRGANOX 245

Time to reach a conductivity of 200 micro Siemens/cm
Correlation between DHC and molding

• DHC measurements reflect the first phase in the degradation process of PVC; it is based on the release of HCl from the PVC resin.

• Measuring the discoloration of PVC resins (e.g. by compression molding) reflects the final stage of the degradation process, involving different degradation mechanisms (DHC and autoxidation)

• A correlation exists between DHC and the discoloration of PVC plaques: the higher the DHC stability, the better the color in the compression test
Conclusion and summary

• Partially hindered phenols show the best performance in thermal stabilization of neat PVC resin (during polymerization, stripping, and drying)

• Partially hindered phenols show, at concentrations needed for good thermal stability of the resin, chain stopping almost as good as ATSC

• Good correlation between DHC (HCl release) and compression molding (discoloration)
Thank you for your attention!

Please visit our internet site:

www.cibasc.com

For further information, please contact:

Alex Wegmann
Application Technology
alex.wegmann@cibasc.com

Shandy Li
Application Technology
shandy.li@cibasc.com

Thank you for your attention!