ELUCIDATING THE CAUSE OF SURFACE ROUGHNESS IN MELT COMPOUNDED PVC PLASTICIZED BY HIGH-SOLVATORS

Brad L. Farrell, William D. Arendt, Emily L. McBride
Emerald Kalama Chemical, LLC
Kalama, Washington

Abstract

High-solvating plasticizers, like dibenzoates, have shown marked success in their ability to plasticize PVC. This unique interaction has proven beneficial for formulators as dibenzoates are fast-fusing at lower temperatures, decreasing time and energy costs during processing. However, when plasticizers are used in processing conditions involving high shear, a characteristic surface roughness or, “nerviness” can be observed on a two roll mill. Using FTIR, gelation studies, tensile data and gloss measurements, this investigation aims to determine the cause of this morphology. The results indicate that secondary crystallite formation is likely the cause of the nervousness observed in flexible PVC. As well, nerviness was manifested formulations plasticized with DINP, and 1,2-cyclohexanedicarboxylic acid diisononylphthalate (DIDC), suggesting nerviness is an inherent phenomenon with PVC fusion that shifts to lower processing temperatures with high-solvating plasticizers.

Introduction

Surface roughness in melt-compounded and extruded PVC products is well known. Summers observed this phenomenon in extruded PVC and attributed it to melt flow inconsistencies after viewing acetone-swelled samples on an electron microscope.¹ It was claimed that at low temperatures there is little cohesiveness between melt flow units and they consequently flow through the die independently. As temperature increases, weak interactions begin to occur but when shear is applied, they easily tear apart, creating “nerviness.” At high temperatures, these interactions are strong enough to produce a smooth, cohesive article.

This theory was later expanded upon to assert that nerviness is caused by secondary crystallite formation.² As PVC is milled, primary particles begin to gel in which secondary crystallites are the tie points between them. Failure to re-melt these crystalline regions when shear is applied prevents flow, causing considerable melt fracture. At high processing temperatures the nerviness subsides, as the crystallites begin to melt. The melting point of these crystallites can be lowered in plasticized PVC, as the plasticizer can have a solvent effect at processing temperatures.³

The degree of this solvation process depends largely on the interaction between the PVC and plasticizer. This compatibility is empirically quantified by the Flory-Huggins interaction parameter (X).⁴ Dibenzoates, due to their polarity, have a much stronger interaction with PVC than GP phthalates, like DINP. 1,2-Propylene glycol dibenzoate has an interaction parameter of ~0.10, and dipropylene glycol dibenzoate is slightly higher at 0.37, far exceeding the compatibility range of most phthalates (~0.5-0.8).⁵ One would predict then that high solvators, like dibenzoates, substantially lower the melting point of PVC crystallites as compared to GP phthalates, producing nerve at lower temperatures. This would allow for decreased processing temperatures using high solvators compared to GP phthalates.

The study of this dynamic is complicated by the notoriously difficult measurement of crystallinity in PVC. Even stand-alone flagship methods of determining polymer crystallinity like wide-angle X-ray diffraction (WAXD) can produce inaccurate results in plasticized PVC.⁶ Witenhafer et. al proposed using infrared spectra to determine relative crystallinity, but this involved the cumbersome process of polymerizing vinyl chloride in the presence of a urea complex.⁷ This method was improved upon by Koenig where a crystallinity index in plasticized PVC was measured by digitally subtracting the neat plasticizer spectra from the plasticized sample.⁸ It was determined that the methylene deformation absorbance at 1427 cm⁻¹ and 1435 cm⁻¹ are assigned to the crystalline and amorphous bands, respectively. The ratio of these (I₁₄₂⁷/I₁₄₃₅) gives a relative crystallinity index of the bulk sample which can be used to establish a relationship to nerve.

This investigation aims to elucidate the processing temperature range that causes surface nerve in sheets plasticized with dibenzoates by studying relative crystallinity, gelation, tensile/elongation, and gloss measurements. These values will be compared in PVC sheets plasticized with a GP phthalate, diisononylphthalate (DINP) versus a blend of diethylene glycol dibenzoate, dipropylene glycol dibenzoate and propylene glycol dibenzoate (975P). Attempts will be made to correlate these crystallinity values to nerve and the processing temperature dependence on nerviness will be investigated. Finally, the dynamics between plasticizer...
interaction parameter and nervy onset temperature will be studied.

**Materials**

This study involves the use of four plasticizers, a general purpose (GP) type, diisononylphthalate (DINP), a GP phthalate alternative, DIDC and two dibenzoate plasticizers, a mixture of diethylene glycol dibenzoate, dipropylene glycol dibenzoate and propylene glycol dibenzoate (975P), and propylene glycol dibenzoate (PG). A suspension PVC resin was utilized for all samples.

**Preparation of Formulations:** The dry components PVC and stearic acid, were added a mixing bowl (Table 1) and slowly stirred for 1 minute. In a separate vessel, the plasticizer and stabilizer were until homogenous. While stirring vigorously, liquid components were slowly poured into mixing bowl with the dry components and mixed using a planetary mixer at low speed for 10 minutes at 170°F to make a dry blend.

**Percent Gelation Studies: Milled** samples were weighed on an analytical balance and prepared inside T-Zero aluminum pans. These were run in a TA instruments Q200 Differential Scanning Calorimeter from 0°C to 220°C at 10°C/min. N₂ flow rate = 50 mL/min.

**Formulation Melt Compounding:** Using a LabTech LRMR-S-150/0 2-roll mill equipped with an LOH-9000 oil heating unit, formulations (400 g) were charged onto the rollers (initial nip-gap 1 mm, 1:1:1 roll speed ratio). Samples were banded at 2 min, 4 min, and 5 min, then calendered for an additional 1 min for a total 6 min milling time.

**Crystallinity Determination:** Thin specimens were cut from milled samples and placed on a Thermo-Scientific Nicolet iS50 equipped with an AHR accessory (32 scans, resolution = 4 cm⁻¹).

**Gloss Testing:** 60° Gloss measurements were taken by a BYK Micro-Tri-Gloss glossmeter. Readings were repeated x3.

**Tensile Testing:** Milled samples were cut by a Schmidt Press using an ASTM D638 type IV die. These were loaded into an Instru-Met tensometer equipped with a 200lb Sn 1829 load cell and pulled at 2 in/min in accordance with ASTM D638. Tensile tests were replicated x6 per sample to achieve low standard deviation.

**Discussion**

To elucidate the effect of mill temperature on nervous, the DINP and 975P samples were milled between 120°C and 200°C in 10°C increments (Fig. 1). Each sample was rated on a “nerviness scale” from 1-10 (1 = low nerviness) and as surface roughness affects specular reflectance, gloss measurements were taken to quantify the nerviness (Fig. 2). Low temperature milling resulted in a dull, smooth sheet while high temperatures produced a glossy smooth sheet. The intermediate temperatures generated severe nerviness. 975P plasticized sheets had a nervy onset temperature of ~140°C while DINP was shifted toward a higher temperature at 160°C. The same trend was observed at the temperature at which nerviness subsided where 975P decreased at 180°C and DINP at 190°C.

A tensile ladder was performed to elucidate the tensile strength and elongation of each milled sample. Samples were milled at increasing temperature and overall, 975P had higher tensile strength than DINP across the entire temperature range (Fig. 4). As well, there was a slight decrease in tensile and elongation in each plasticizer’s nervy region. This could be due to the large amount of melt fracture occurring or, more likely, is an artifact due to the non-uniform sample thickness in the milled stock from the nervy region.

To explore whether the higher tensile strength observed in 975P plasticized sheets was due to higher crystallinity, and its relationship to nerviness, samples were milled at 150°C and were quenched immediately into liquid N₂ to crystallinity analysis. These were measured on an FTIR spectrometer and each respective plasticizer spectra was subtracted to deconvolute the crystalline and amorphous methylene bands at 1427 cm⁻¹ and 1435 cm⁻¹ and a crystallinity index (I₁₄₂₇/I₁₄₃₅) was assigned to each sample (Fig. 3). Additionally, non-quenched samples were measured to ascertain that the quenching method used was effective. Lower crystallinity was observed in both the quenched and non-quenched samples. The 975P plasticized sheet had an I₁₄₂₇/I₁₄₃₅ of 0.99 while DINP was higher at 1.05. This suggests that the high-solvating power of 975P is partially solvating more of the PVC primary crystallites than DINP. As FTIR is likely only revealing primary crystallinity due to tactility, secondary crystallite formation was investigated by gelation degree.

The degree of crystallite gelation was calculated by integrating the endothermic response due to the melting of partially gelled crystallites (Area A) and the endothermic response due to crystallites that were not gelled in processing (Area B) (Fig. 5): Percent gelation was calculated by applying the formula: ¹⁰

\[
\% \text{ Crystallite Gelation} = \frac{\text{Area A}}{\text{Area A + Area B}} \times 100
\]

Across the entire processing temperature range (130°C to 190°C), 975P plasticized sheets showed an overall greater percent crystallite gelation over DINP plasticized sheets.
This, together with the FTIR data suggests that the high tensile strength and elongation observed in dibenzoates occurs because of high degrees of gelation and decreased primary crystallinity. It is reasonable to assume then that dibenzoates lower the melting temperature of PVC secondary crystallites.

As the solvency of the plasticizer plays a substantial role in the melting temperature of secondary crystallites, experiments were run to correlate interaction parameter (X) and nerviness onset temperature. Sheets were prepared with 3-phenylpropanyl benzoate (X = -0.26), propylene glycol dibenzoate (X = -0.1) and 1,2-cyclohexanedicarboxylic acid diisononylphthalate (referred to generically as DIDC, X =1.04). The onset of nerviness for the 3-phenylpropanyl benzoate plasticized sheet was 130°C while DIDC was at 170°C. Pairing this with the nerviness onset temperatures for 975P (X = 0.36) and DINP (X= 0.70), at 140°C and 160°C, respectively, there is an apparent relationship between plasticizer interaction parameter and the nerviness onset temperature. This suggests that at low X values, the plasticizer has high solvent properties at processing temperatures, decreasing the melting point of secondary crystallites. High X-values imply low crystallite interaction. Nerviness observed in melt-compounded and extruded PVC seems to be exclusively dictated by temperature independent of shear rate. Attempts were made to reduce nerviness isothermally with additives but were unsuccessful. As well, nerviness onset temperature in flexible PVC can be controlled by adding a high solvating dibenzoates which has the lowest nerviness onset and declination temperatures, which can be beneficial for processing PVC.

**Conclusions**

The intent of this investigation was to determine the temperature dependence of undesired nerviness found in dibenzoate-plasticized sheets and to explore options to eliminate it. This phenomenon was found to be temperature-related, not unique to dibenzoates, but rather an event that occurs in all plasticized sheets, suggesting this is an inherent feature of PVC fusion when shear is used alongside temperature to fuse the PVC. The temperature of nerviness onset was dictated by the plasticizer species, presumably due to partial solvation of secondary crystallites by the plasticizer. Nerviness onset was simply shifted to a lower temperature when plasticized with dibenzoates. FTIR and DSC suggested lower primary crystallinity and higher gelation in the bulk product over DINP sheets. These unique interactions demonstrate the lower processing characteristics of high-solvators, while producing a product capable of higher tensile strength and elongation.

**Acknowledgment**

The authors acknowledge Dr. Stephen Foster, Sarah Strother, Debra Davidson, and Kyle Posselt with their assistance in experiments, calculations and sample preparation. In addition, product samples were kindly provided by Formosa Plastics and Galata Chemicals.

**Disclaimer**

The information contained herein is believed to be reliable, however is based upon laboratory work with small scale equipment and does not necessarily indicate end-product performance. Because of variations in methods, conditions and equipment used commercially in processing these materials, Emerald makes no representations, warranties or guarantees, express or implied, as to the suitability of the products for particular applications, including those disclosed, or the results to be obtained. Full-scale testing and end-product performance are the responsibility of the user. Emerald Performance Materials shall not be liable for and the customer assumes all risk and liability for use and handling of any materials beyond Emerald’s direct control. Nothing contained herein is to be considered as permission, recommendation nor as inducement to practice any patented invention without permission of the patent owner.

**References**


Appendix

Table 1. Formulations Used For Testing.

<table>
<thead>
<tr>
<th>Formulation Name</th>
<th>PHR</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 K-68 PVC Resin</td>
<td>100</td>
</tr>
<tr>
<td>2 Stearic Acid</td>
<td>1</td>
</tr>
<tr>
<td>3 Plasticizer</td>
<td>70</td>
</tr>
<tr>
<td>4 Ca/Zn Stabilizer</td>
<td>3</td>
</tr>
</tbody>
</table>

Figure 1. Temperature dependence surface nerve, where low temperatures yield a smooth, dull sheet while intermediate temperatures produce a nervy sheet. High milling temperatures eliminate nerve.

Figure 2. Nerviness ratings and 60° gloss measurements. The temperatures producing nerviness can be considered as the area in between the two crossover points.
Figure 3. Quenched FTIR comparison of 975P and DINP. Overall there is lower crystallinity in the samples plasticized with 975P than those with DINP.

Figure 4. Tensile strength (left) and elongation (right) of 975P and DINP samples. 975P provides the same tensile strength as DINP at lower temperatures.

Figure 5. DSC measurements of PVC % gelation. Sheets plasticized with 975P showed a higher gelation than those plasticized with DINP across the entire processing temperature range.