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Novel Plasticizers for Low Fusion Temperature Plastisols

Presented by
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Background

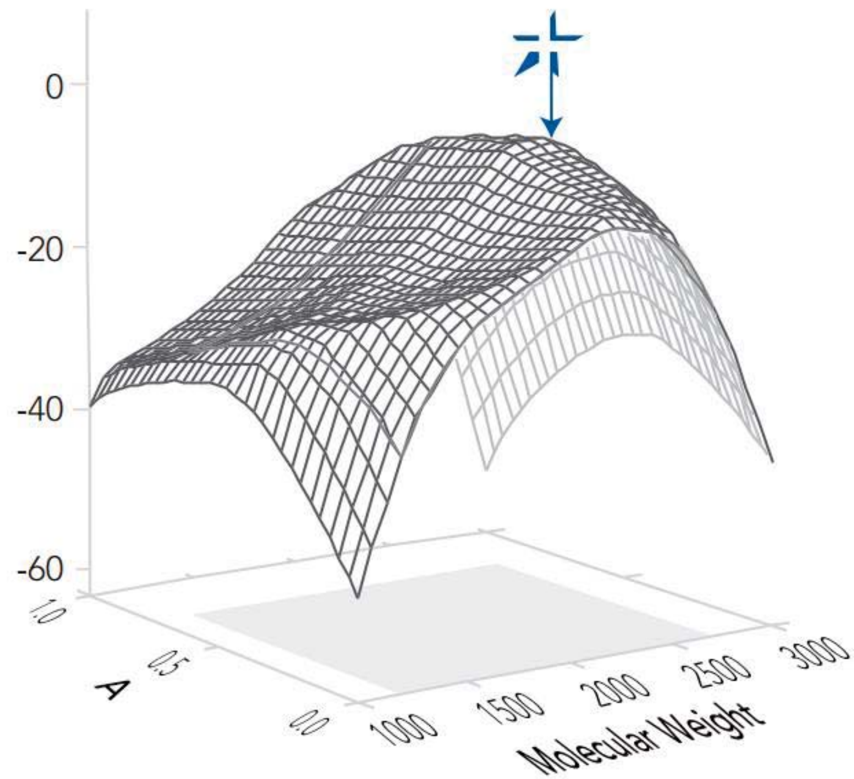
Plastisols are widely used for their utility and ease of processing. Therefore, plasticizers capable of lowering the gelation/fusion temperature of the plastisol are highly desired.

Although low gelation and fusion temperatures are sometimes the main drivers for plasticizer selection, compounders also put high value on permanence, low migration and weight loss.

Project Introduction

In this study, we investigated the structure-property relationship (SPR) between common plasticizers in low-fusion plastisols with Hallstar's modified polyester adipate products.

Test data includes gelation/fusion temperatures by both hot bench and rotational rheometer methods.



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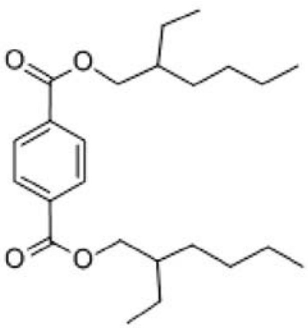
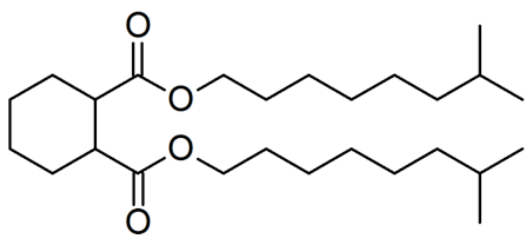
Focus of the Project

Hallstar has developed a line of phthalate-free plasticizers for PVC plastisols. The focus of this project is to investigate how chemical modification of the plasticizer structure would affect gelation/fusion temperatures of the plastisol.

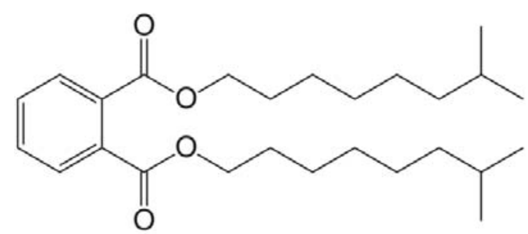
Dioctyl terephthalate (DOTP)
CAS# 6422-86-2



1,2-Cyclohexane dicarboxylic acid diisononyl ester (DINCH)
CAS# 166412-78-8



Diisononyl phthalate (DINP)
CAS# 68515-48-0



Focus of the Project

Hallstar has developed a phthalate-free, low-molecular weight, polyadipate plasticizer (RX-14469) for low fusion plastisols. In this study, we further modified the chemical structure of this plasticizer to improve solvency between the polyester and the PVC resin.

We conducted a side by side evaluation of the modified polyadipates versus commonly used plasticizers in the PVC plastisol industry, such as phthalates, alkylsulfonate, and dibenzoates as low-fusion alternatives.

Our goal is to better understand the structure property relationships between plasticizer structure and how modifying the structure of a polyester affects basic plastisol properties.

Experimental Formula

Formula	1	2	3	4	5	6	7	8
Geon 121A	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Thermchek 904	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0
Paraplex G-62	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0
RX-14469	100.0	---	---	---	---	---	---	---
RX-14607	---	100.0	---	---	---	---	---	---
RX-14508	---	---	100.0	---	---	---	---	---
DOTP	---	---	---	100.0	---	---	---	---
DINCH	---	---	---	---	100.0	---	---	---
DINP	---	---	---	---	---	100.0	---	---
Alkylsulfonate	---	---	---	---	---	---	100.0	---
Dibenzoate	---	---	---	---	---	---	---	100.0

For this experiment, we used PolyOne's Geon 121A as the base resin. This high-molecular weight resin was chosen for excellent mechanical properties and good dispersability for simplified plastisol preparation.

Plastisol Preparation

- Weigh out raw material in mixing bowl
  - Mix using KitchenAid whisk (20 minutes)
- Transfer material to vacuum chamber
  - Attach agitator and mix (30 minutes)
  - Pull vacuum on plastisol
  - 1 mm Hg (30 minutes)
- Transfer to container for plastisol evaluation

Hot Bench Gelation Temperature Procedure

- In this test method, a plastisol is drawn down across a temperature gradient.
- Aluminum foil is brushed onto plastisol for 30 seconds, then removed.
- Temperature reading are taken where the material is no longer tacky (gelation temperature).

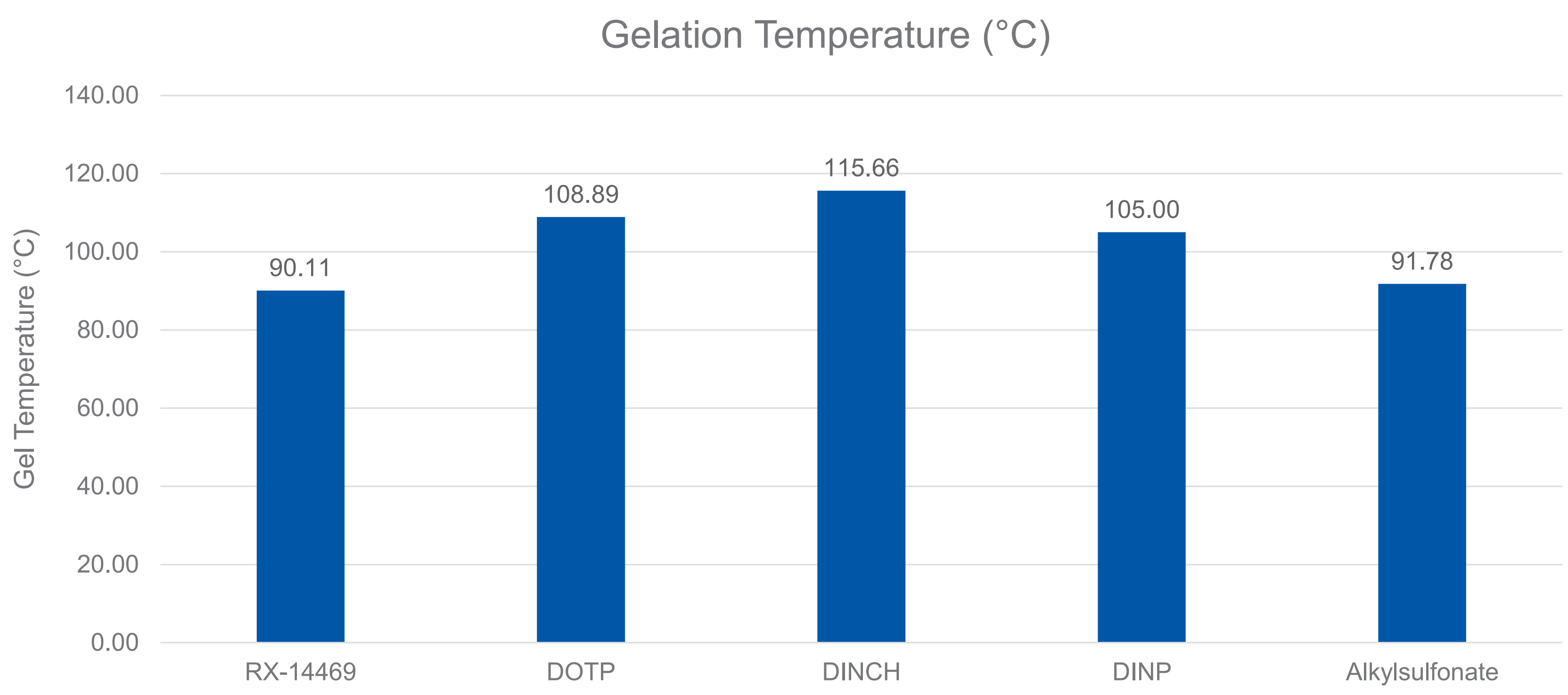
Advantages

- Quick procedure
- Inexpensive

Disadvantages

- Subjective visual measurement
- Limited temperature range

Hot Bench Gelation Temperature



New Equipment for Plastisol Gel Temperature

Advantages

- Complete gelation and fusion profile
- Reproducibility
- Ease of use
- Accurate measurements

Disadvantages

- Expensive equipment

Malvern Lab + Rheometer

Test Specifications	
Geometry	20 mm Parallel Plate
Temperature Range	40-200°C
Temperature Ramp Rate	5°/minute
Gap Width	.5 mm
Oscillation Frequency	1 Hz

Byong Yong Yu, Ah Reum Lee, Seung-Yeop Kwak
“Gelation/fusion behavior of PVC plastisol with a cyclodextrin derivative and an anti-migration plasticizer in flexible PVC”
European Polymer Journol 48 (2012) 885-895

Rheometer Data Interpretation

G' (storage modulus)

Measures the stored energy from an applied stress/strain and represents the elastic portion of the viscoelastic material.

G" (loss modulus)

Measures the energy dissipated as heat from an applied stress/strain and represents the viscous portion of the viscoelastic material.

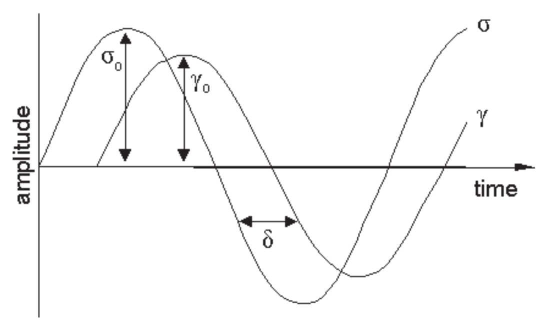
Phase angle (δ)

Shift from the applied stress/strain to the response of the material. When the phase angle is 45° (Tan(δ)=1), the material is transitioning into a gel

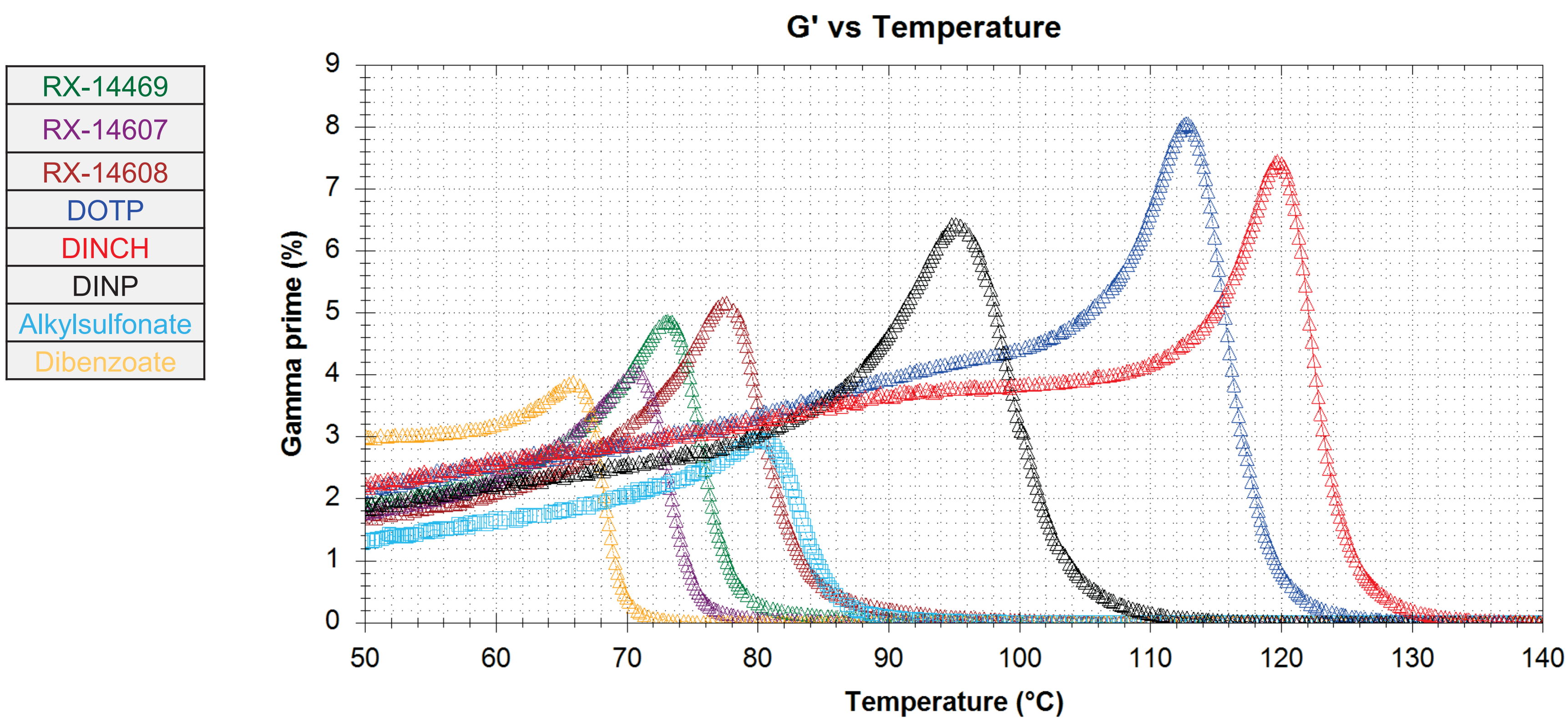
δ=0° (Hookean solid)

δ=45° (Gel Temperature)

δ=90° (Newtonian Fluid)



Rheometer G’ Data (Storage Modulus)



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Rheology Explanation

- Temperature at which G' and G" first cross is considered the gelation temperature. This is the point where the plasticizer swells the PVC resin resulting in a loss of tack/increased viscosity.

- Above the gelation temperature, both the G' and G" decrease. In this region, PVC loses its granular morphology and begins fusion. Rapidly changing G' and G'' can result in some distortion. Until the second G'/G'' crossover, the material behaves as a viscoelastic solid with a phase angle less than 45°

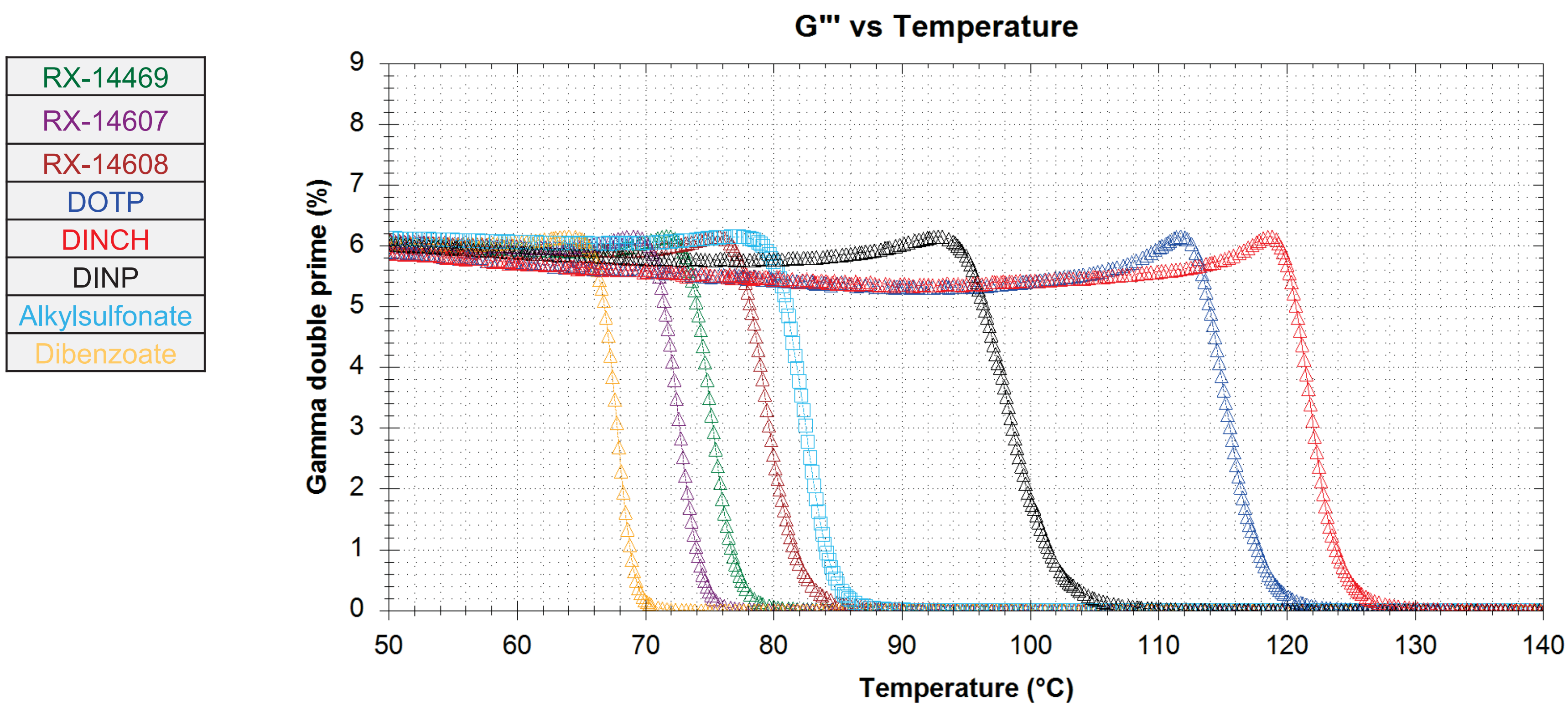
$\delta=0°$ (Hookean solid)

$\delta=45°$ (Gel Temperature)

$\delta=90°$ (Newtonian Fluid)

Jacques Verdu, Agnes Zoller, Antonio Marcilla. "Plastisol Gelation and Fusion Rheological Aspects" Journal of Applied Polymer Science, Wiley, 2013, 129, pp 2840-2847

Rheometer G” (Loss Modulus)



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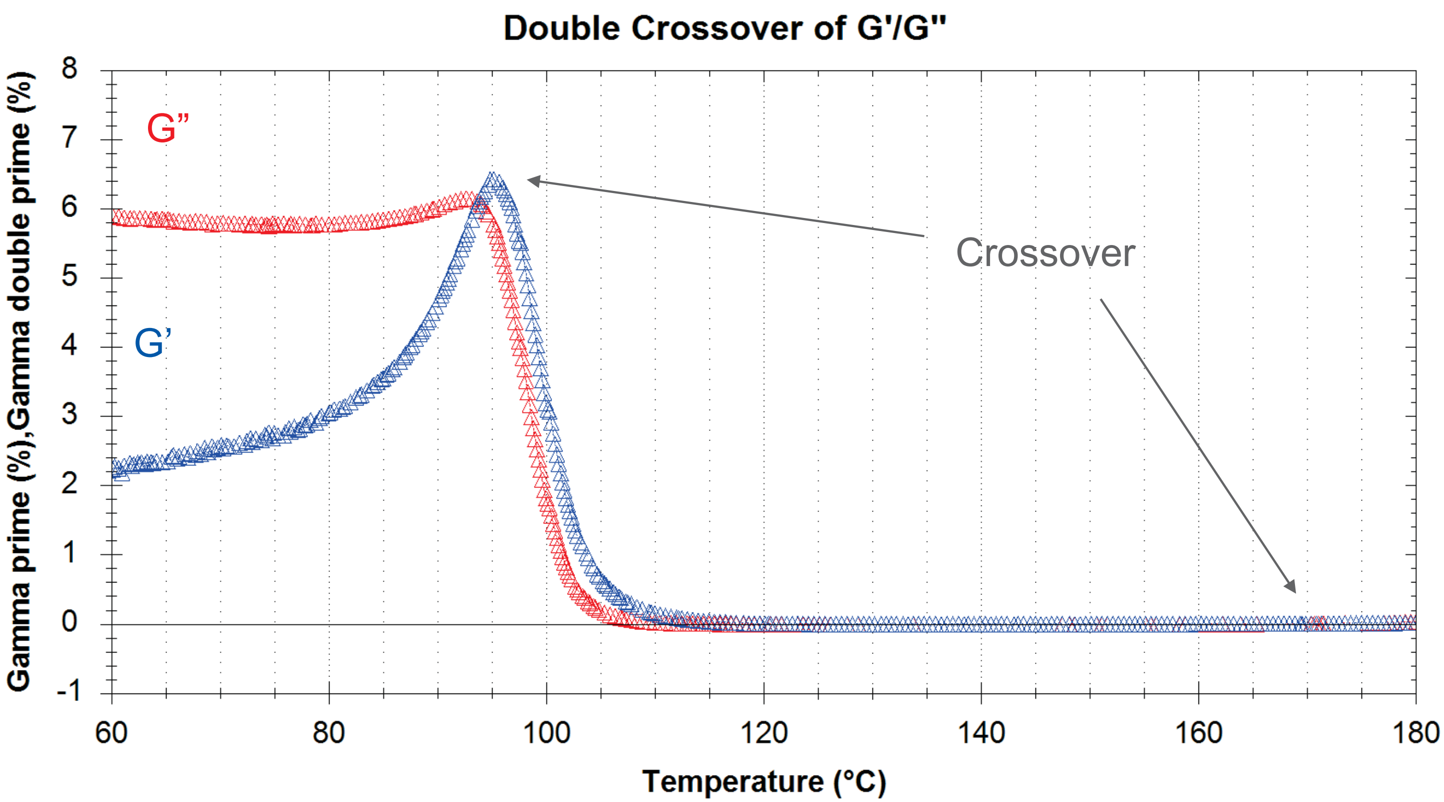
Double Crossover of G' and G" (DINP)



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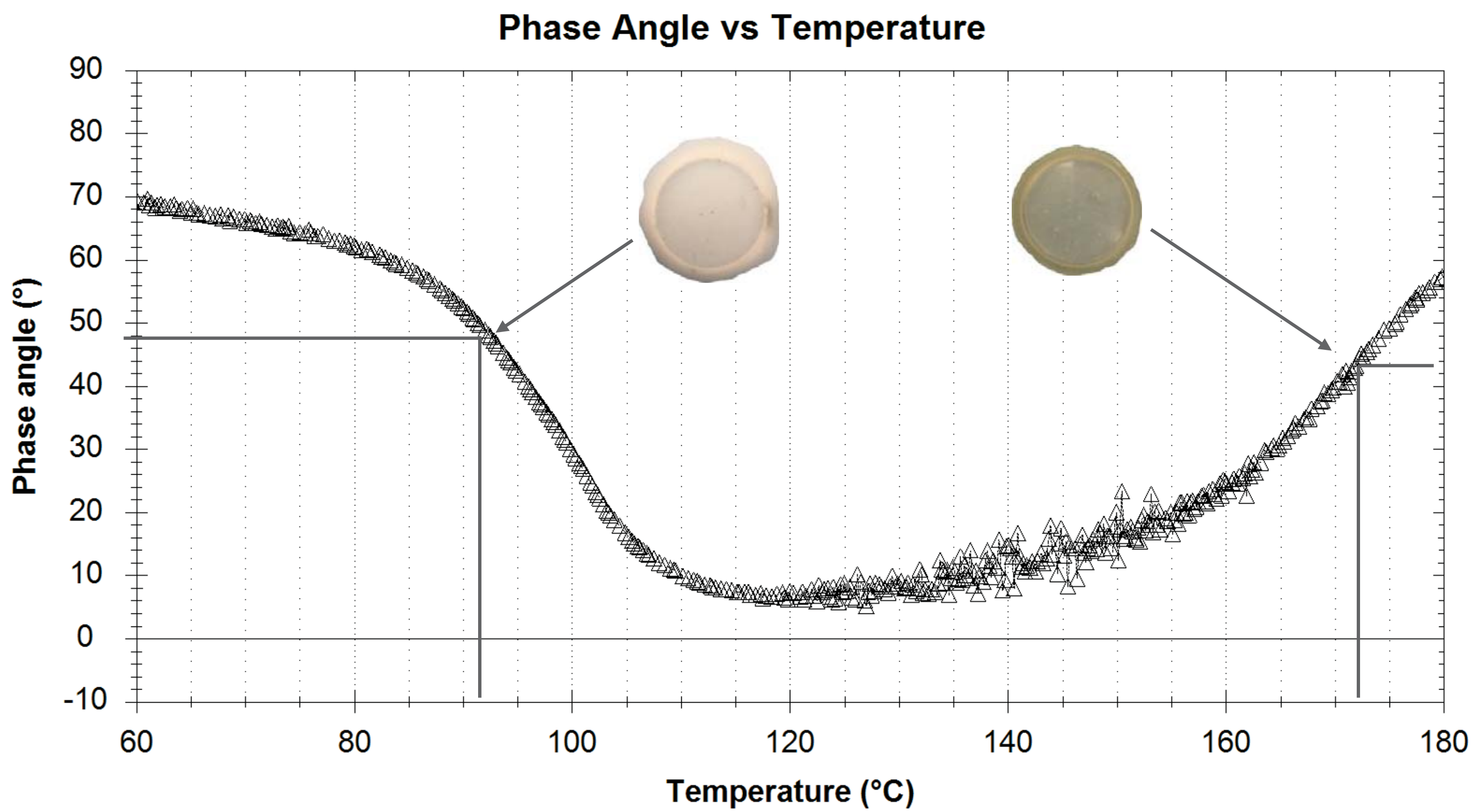
Phase Angle vs Temperature (DINP)



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Rheometer Gelation/Fusion Results

Sample Variable	Gelation Temperature (°C)	Fusion Temperature (°C)
RX-14469	74.5	170
RX-14607	73	168
RX-14508	78	171.5
DOTP	108	171
DINCH	117	180
DINP	94	173
Alkylsulfonate	83.5	168.5
Dibenzoate	68	164.5

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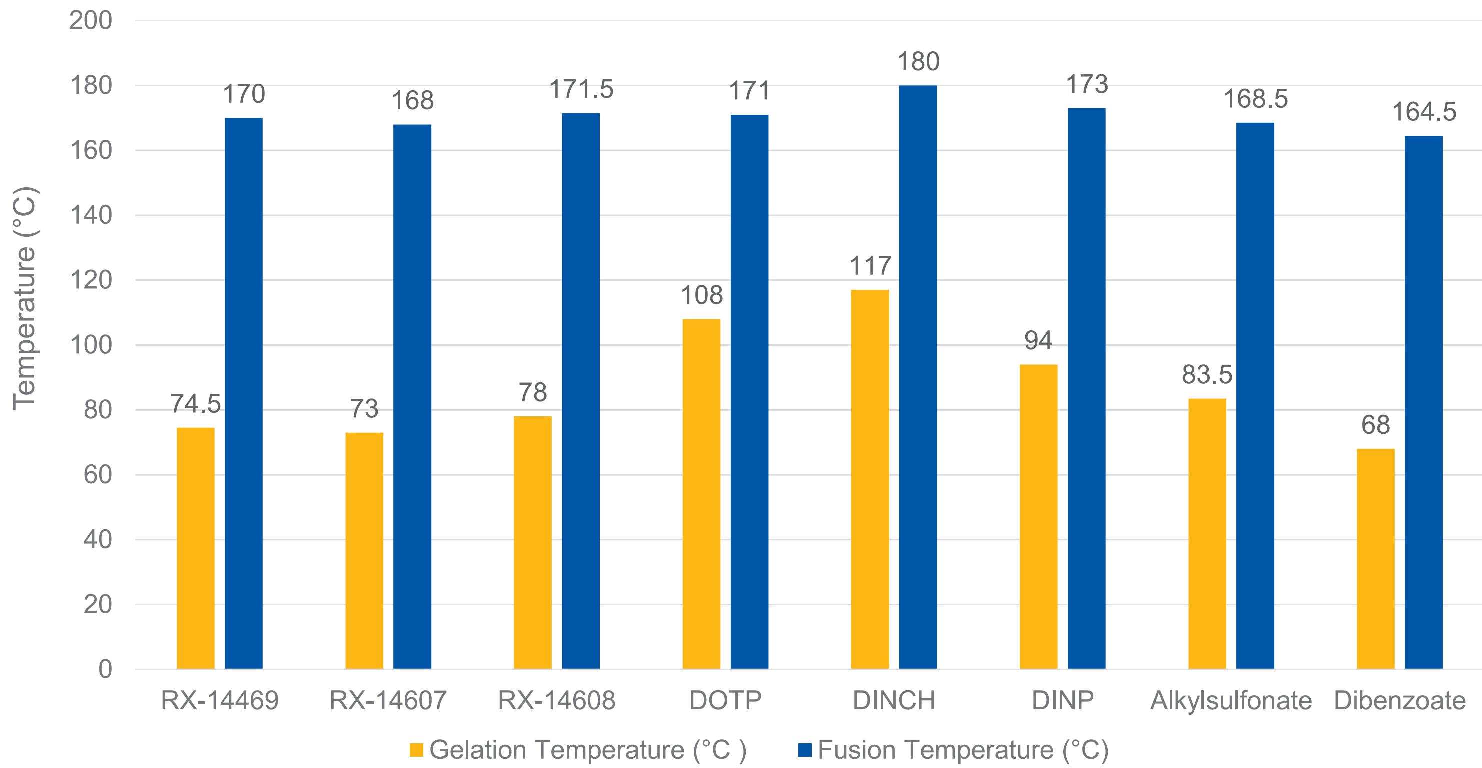
Gelation/Fusion Temperature



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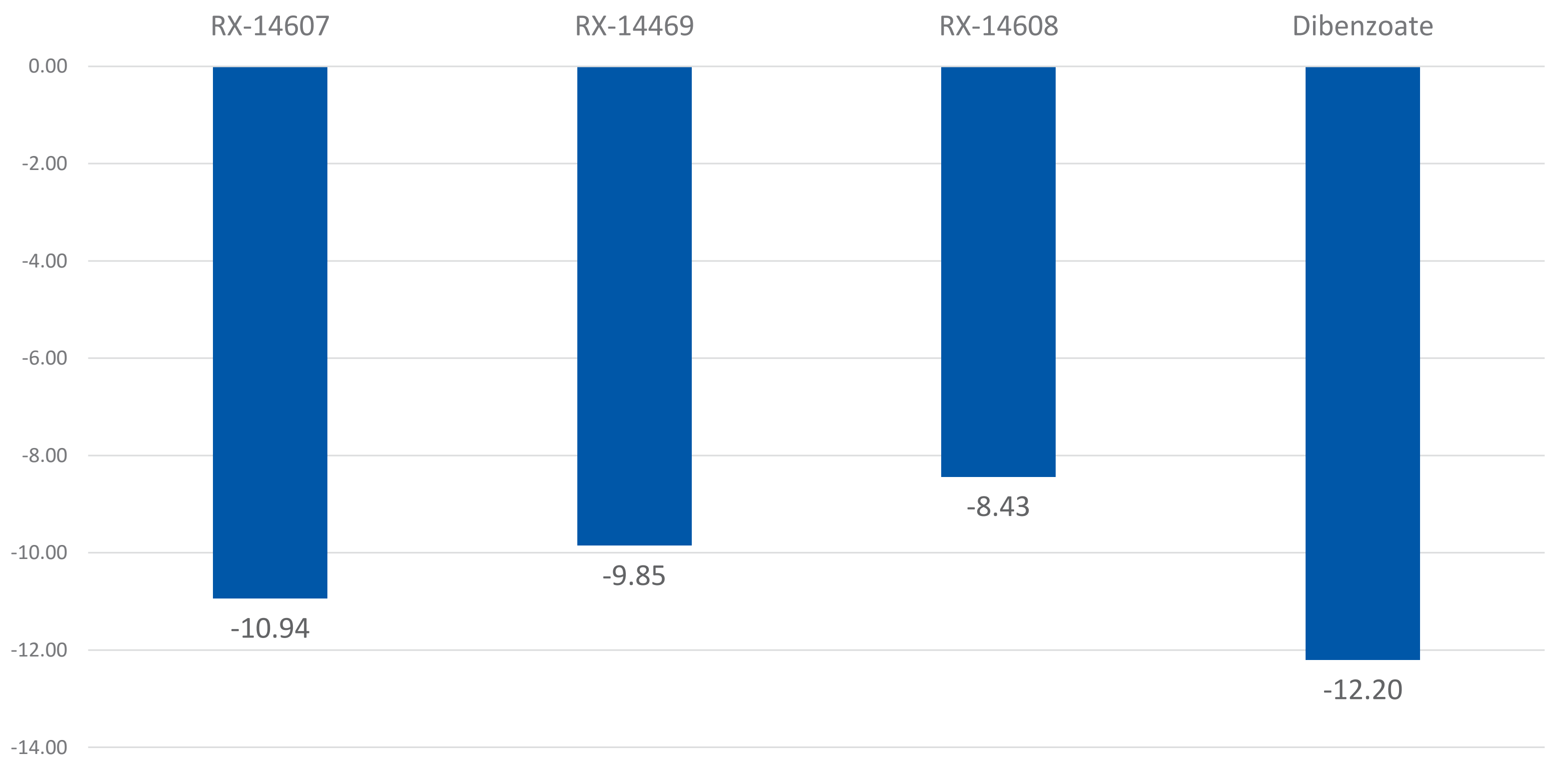
% Weight Loss (70 hours/121°C)



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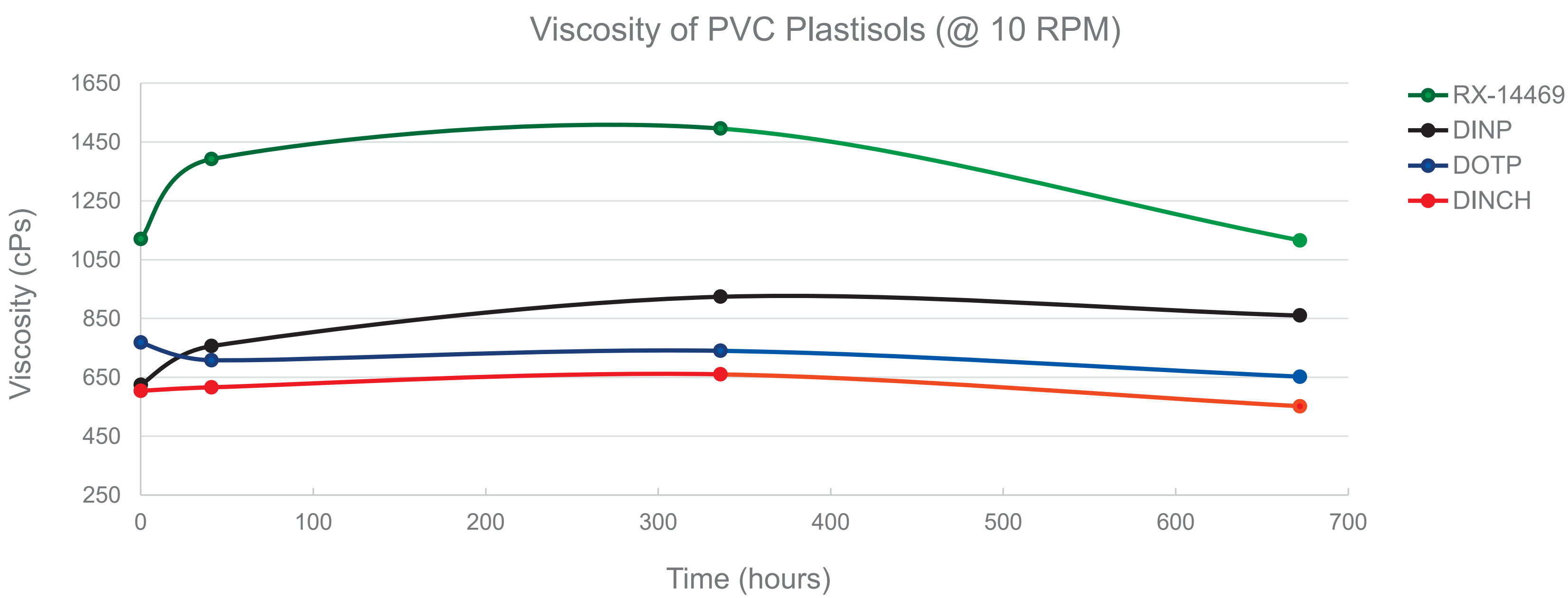
Aged Viscosity of PVC Plastisol



Viscosity (cSt) @ 10 RPM				
Time (hours)	RX-14469	DOTP	DINCH	DINP
0	1120	768	604	624
41	1392	708	616	756
336	1496	740	660	924
672	1116	652	552	860

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Conclusions

- Hallstar's understanding of SPR allowed us to develop low fusion plasticizers capable of outperforming conventional phthalates and alkylsulfonates. Newly developed polyadipates offer a good balance of low gelation/fusion characteristics along with excellent permanence unmatched by dibenzoates.

- SPR analysis and chemical modification of the starting polymeric adipate has shown how changing the structure of the polyester can lead to optimized PVC plastisol performance.

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Thank You

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sneuenfeldt@hallstar.com