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POLYESTER MODIFIERS FOR VINYL FOAM APPLICATIONS

Hallstar Industrial Solutions Company

March 24, 2020

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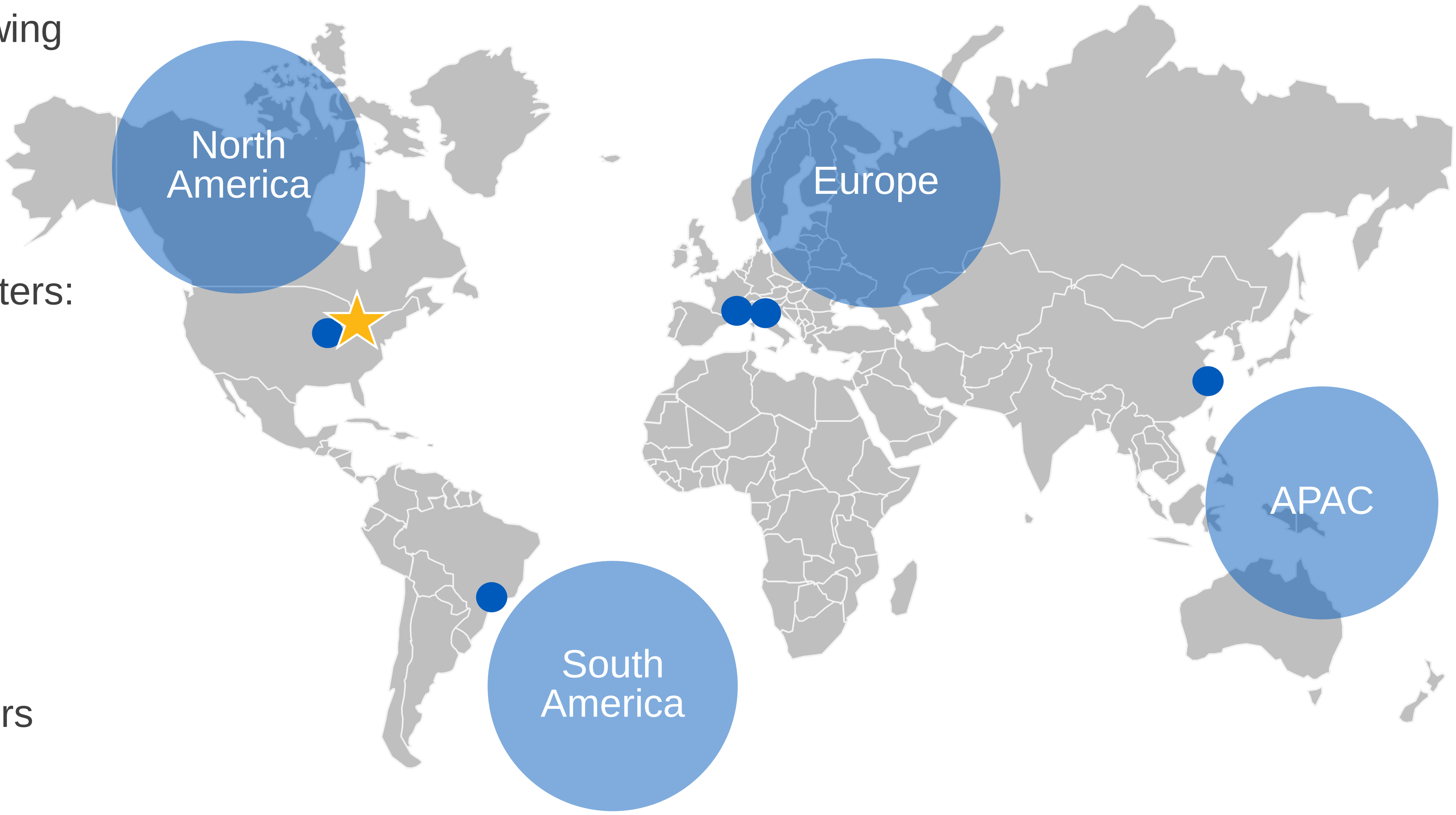
Who is Hallstar?

- Privately-held, rapidly growing mid-market specialty chemical manufacturer
- Corporate headquarters **Chicago, IL, USA**
- 6 R&D/Manufacturing Centers:
    - **Arcore, Italy**
    - **Bedford Park, USA**
    - **Darien, USA**
    - **Jaguariúna, Brazil**
    - **Montpellier, France**
    - **Suzhou, China**
- **200+** Global Team Members
- **100+** Global Patents
- 2 distinct commercial businesses: Industrial and Beauty



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Agenda

Background

Goal of the project

Overview of the experimental plan

Results and discussion

Conclusions

BACKGROUND VINYL FOAMS

Introduction

- The following reasons and performance features drive continuous usage of polymer foams globally:
  - **Light-weight (low density)**
  - **Superb strength-to-weight ratio**
  - **Good insulating capabilities**
  - **Energy absorbing performance**
  - **Comfort features of polymeric foams**
  - **Lower cost (compared to other polymeric composite materials)**
  - **Ease of processing / manufacture**
  - **Flexibility in design**
- Application areas for polymeric foams include, furniture, transportation, bedding, carpeting (underlays), packaging, textiles, toys, gaskets, sport and insulation applications (shoe soles and inserts), appliances, etc.

PVC / Vinyl Foam Classifications

- PVC foams are typically classified on basis of their
  - Flexibility
    - Flexible
    - Rigid
  - Density (*a general guide and ranges shown below*)
    - Low density – 10-50 kg/m^3 (0.6-3.0 lb/ft^3)
    - Medium density – 50-350 kg/m^3 (3-21 lb/ft^3)
    - High density – 350-900 kg/m^3 (21-54 lb/ft^3)
  - Foam cell geometry (nature)
    - Open-cell structure (best for car seating, furniture, bedding and acoustical insulation – typically flexible)
    - Closed-cell structure (best for thermal insulation – typically rigid)
- The nature of the foam cells is very important characteristic, influencing properties, such as
  - Resilience and compression behavior of flexible foam, or
  - Heat conductivity and moisture permeability of rigid foam insulation

GOAL OF THE PROJECT

Goal of the Project

1) Evaluate a polymeric adipate plasticizer in a standard low density vinyl foam formulation
2) Correlate foam performance to the loading level of polyester plasticizer in the total plasticizer loading

Key properties to evaluate:

- Original physical and rheological properties
- Retention of properties after heat-aging
- Fluid extractions resistance (in hexane, DI water and cottonseed oil)
- Low temperature flexibility (Tg by DSC before and after heat ageing)
- Compression set
- DMA analysis before and after heat ageing
- Microscopy analysis of foam samples

OVERVIEW OF THE EXPERIMENTAL PLAN

Vinyl Foam Formulations

Ingredients	PHR LOADING
Inovyn 367NK (PVC Resin)	100
Plasticizer	85
Blowing Agent Mixture *	5

Properties	POLYMERIC ADIPATE
Acid Values (mg KOH/g)	0.4
Hydroxy Value (mg KOH/g)	7
Color (APHA)	133
Viscosity @ 25°C (cP)	976
Moisture (%)	0.02
Specific Gravity	1.065

- *Mixture contains ADC as a blowing agent (25%), Zn-based activator/stabilizer, and carrier*
- *Wet samples 0.025in in thickness were 1) coated on 0.008 in thick release paper, then 2) gelled at 290^{O} F for 2.0 minutes, followed by 3) fusion and blowing at 385^{O} F for 2.5 minutes in an recirculated air convection lab oven.*

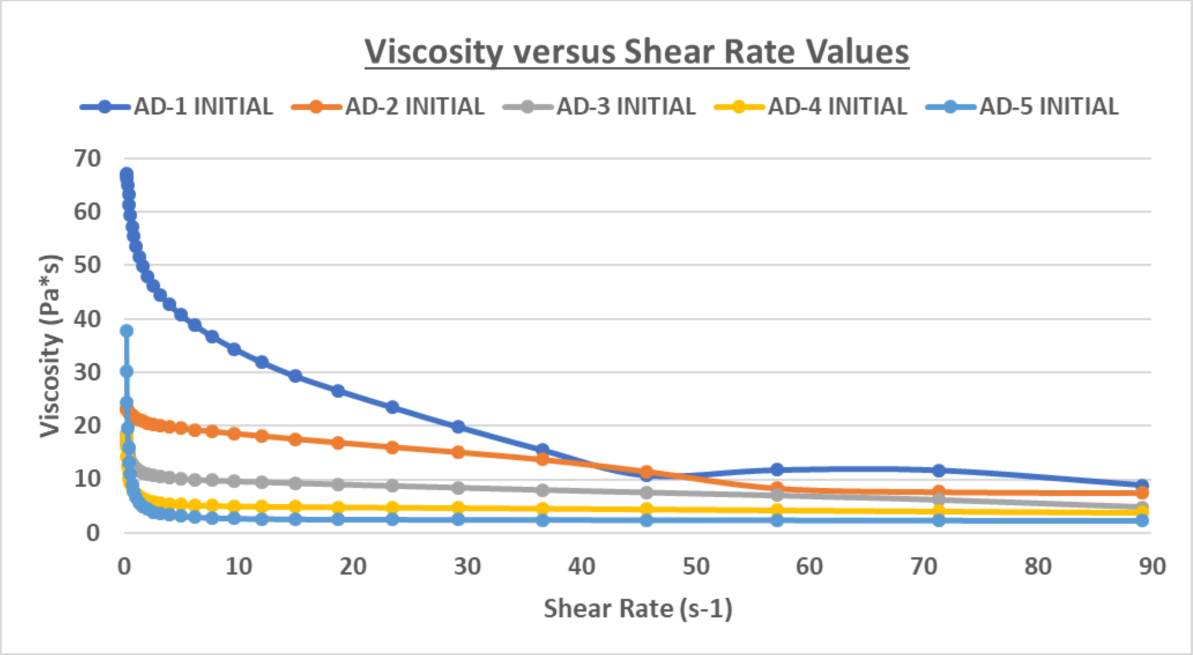
Ingredients	AD-1	AD-2	AD-3	AD-4	AD-5
Inovyn 367NK (PVC Resin)	100	100	100	100	100
DIDP (Monomeric Plasticizer)	0	20	42.5	65	85
Polymeric Adipate Plasticizer	85	65	42.5	20	0
Blowing Agent Mixture	5	5	5	5	5

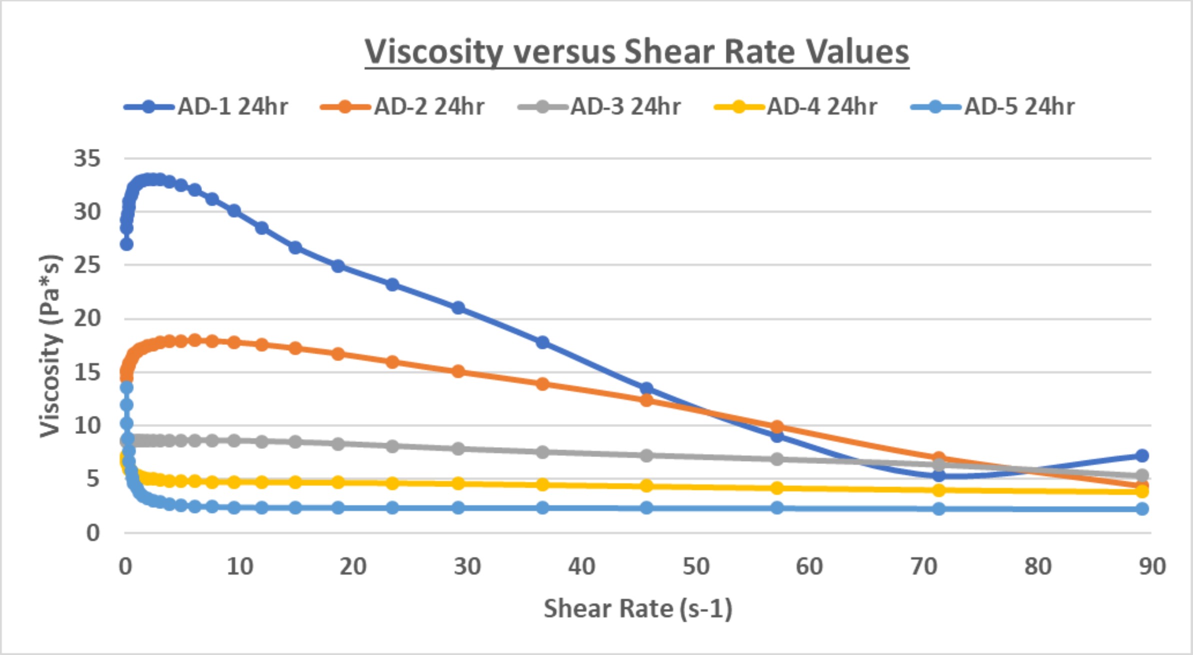
100% Polymeric Adipate Plasticizer

100% DIDP

RESULTS AND DISCUSSION

Plastisol Viscosities of Vinyl Foam Formulations



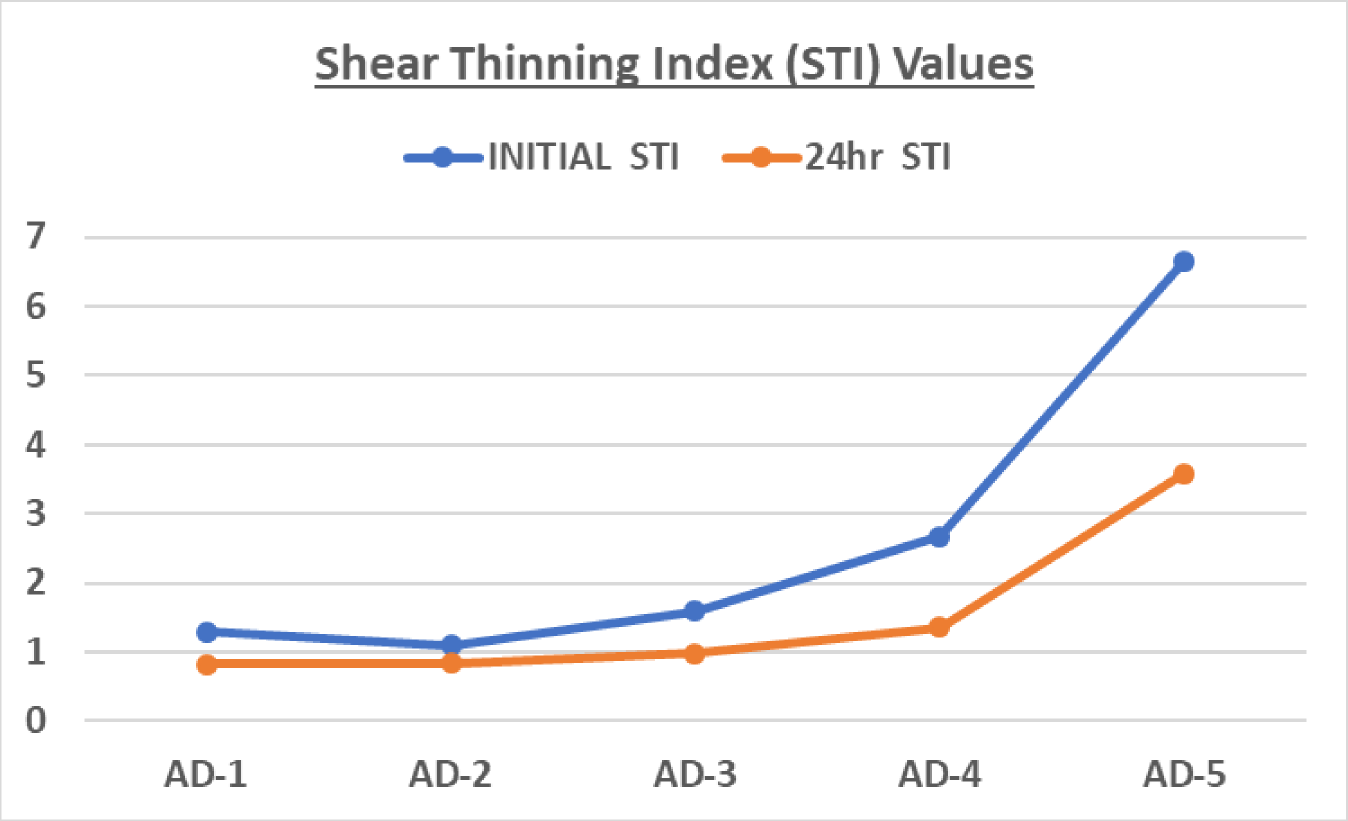


- Initial and 24h plastisol viscosities increase with increasing concentration of polymeric adipate in total plasticizer
- Viscosity values for 24h aged plastisols seem to be lower than the initial viscosities at low shear rates (e.g. less than 10 s^{-1})
- The higher the concentration of polymeric adipate in the total plasticizer, the greater the viscosity differences!

Test Parameters:

- Instrument: Kinexus by Malvern
- Temperature: 25°C
- Gap: Cone & Plate 0.1417 mm
- Shear Rate Range: 0.1 to 100 s^{-1}
- Shear Rate Ramp-Up: Exponential

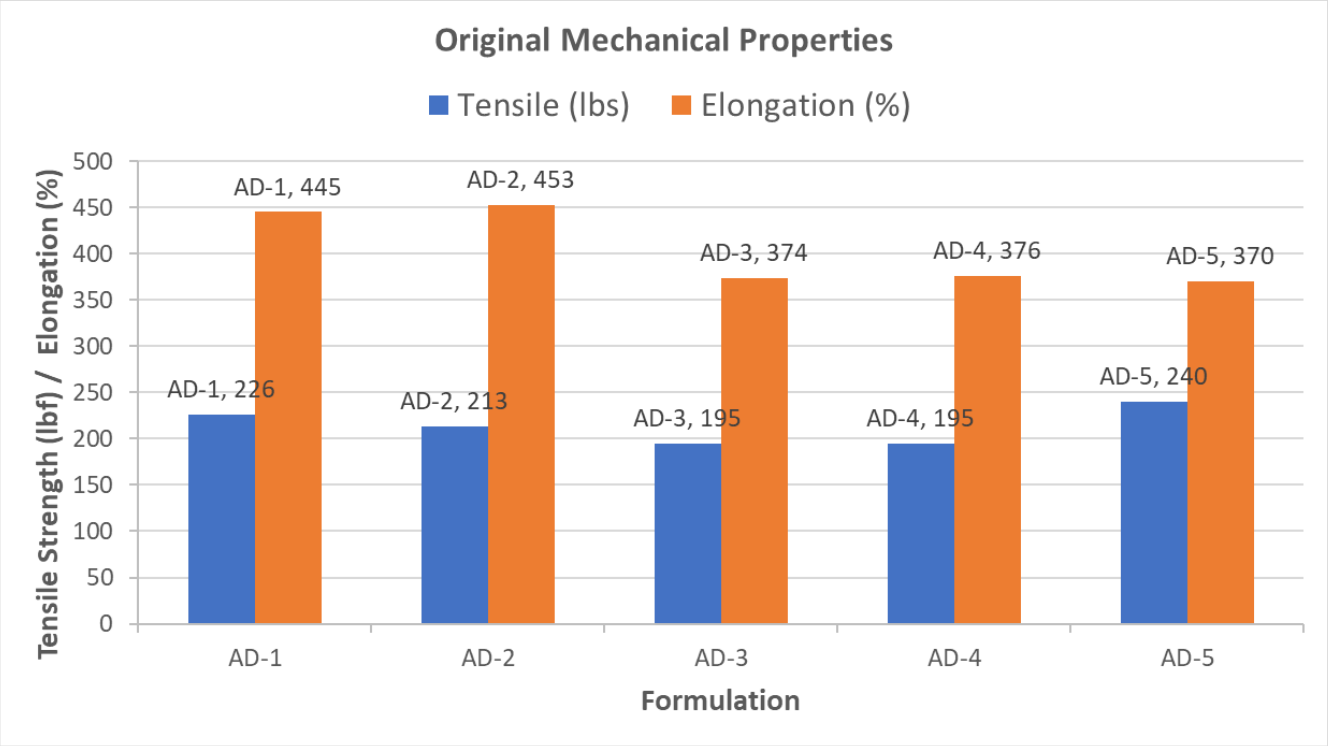
Plastisol Shear Thinning Index (STI) Values



STI values were calculated by dividing viscosity values at 0.1 s^{-1} shear rate with values at 1 s^{-1} shear rate!

- Increasing polymeric adipate concentration reduces STI progressively thus making plastisols less shear-thinning in behavior
- This behavior may be of importance for dipping or coating applications focused on filling cavities and gaps in the substrate
- This drop in STI is apparent even at low levels of polymeric adipate in the total plasticizer
- The 24h STI values are lower than the initial STI values, but the trend remains the same!

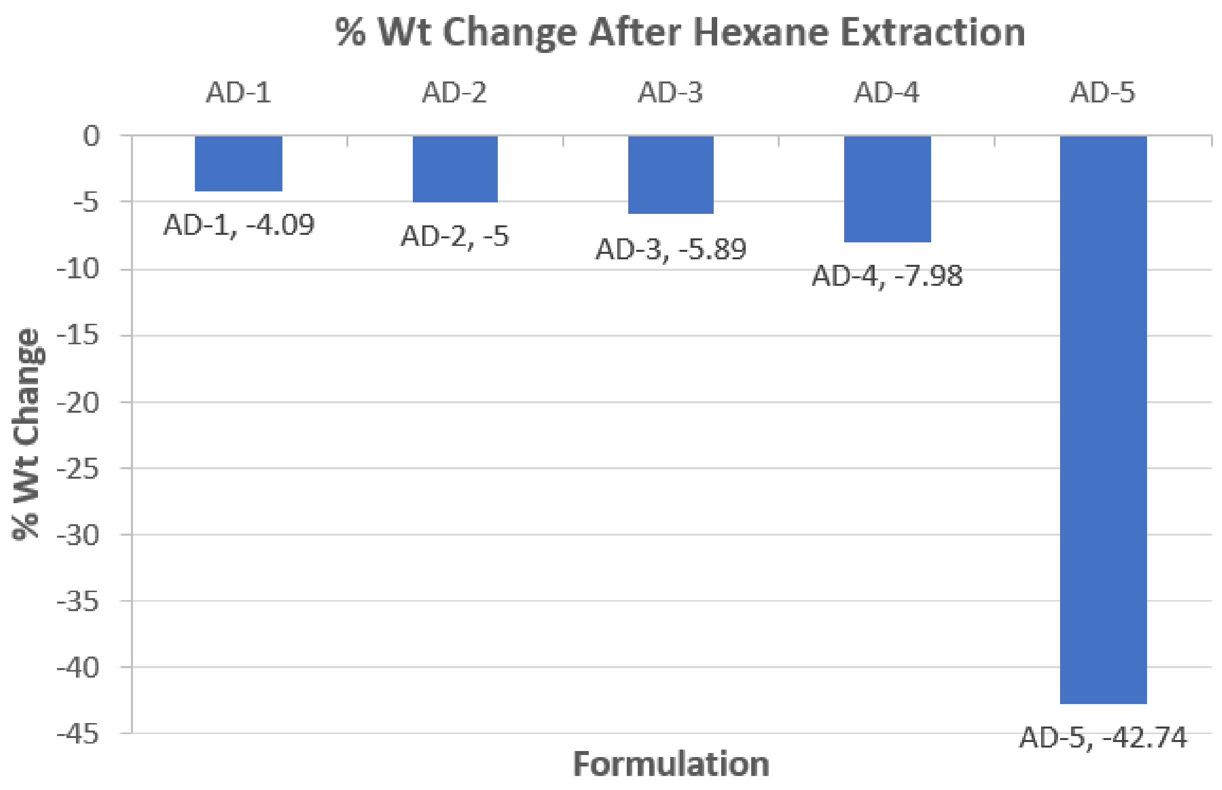
Original Mechanical Properties of Vinyl Foams



Property	AD-1	AD-2	AD-3	AD-4	AD-5
% Polymeric Adipate	**100**	**75**	**50**	**25**	**0**
Tensile (lbf)	226	213	195	195	240
Elongation (%)	445	453	374	376	370

- Increasing polymeric adipate concentration in the total plasticizer increases % Elongation from 370% (AD-5) to about 450% compared to the incumbent based on 100% DIDP (AD-5)
- Tensile Strength of polymeric adipate containing vinyl foams is between 6 and 19% lower than that of the incumbent based on 100% DIDP (AD-5)
- Vinyl foam with higher polymeric adipate loading can hold sustain higher stretching / elongation.

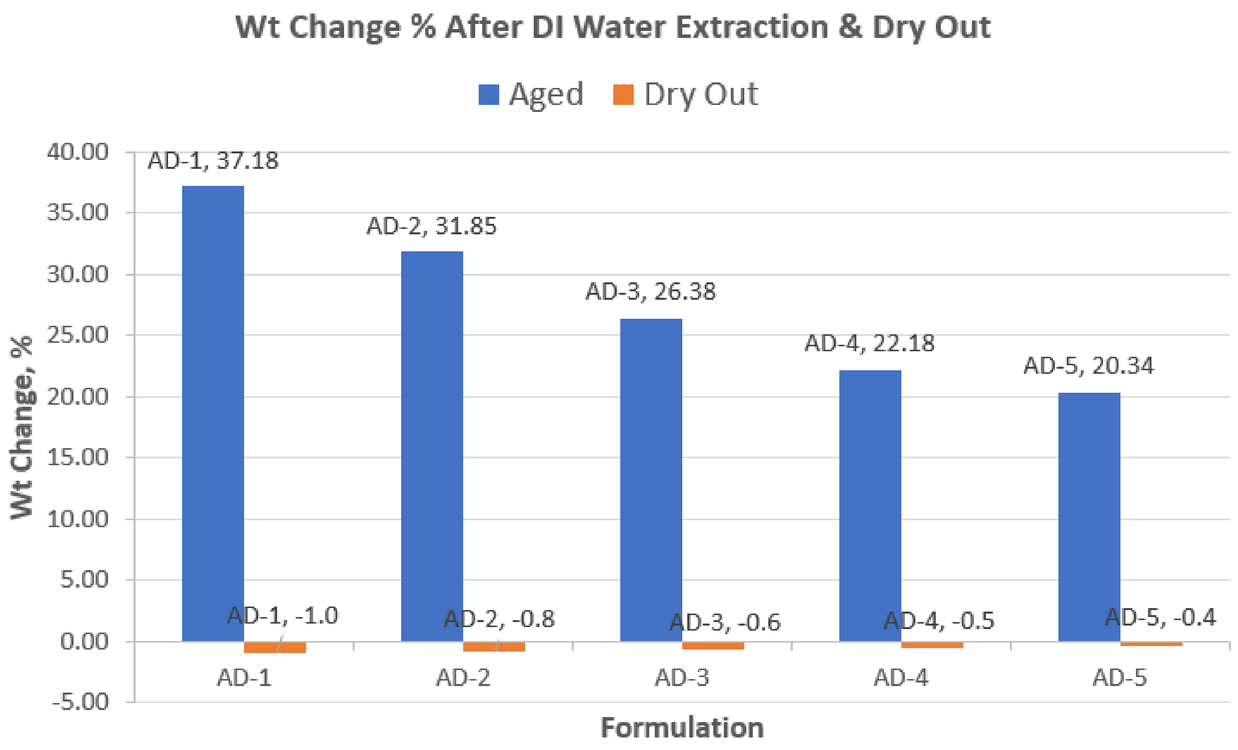
Hexane Extraction Data



Formulation	AD-1	AD-2	AD-3	AD-4	AD-5
% Polymeric Adipate	100	75	50	25	0
% Weight Change	-4.09	-5	-5.89	-7.98	-42.74

- Weight loss after hexane extraction drastically decreases with increasing concentration of polymeric adipate in the total plasticizer
- Considering the sharp drop in weight loss between AD-5 and AD-4 formulations, results indicate that even small levels of polymeric plasticizer would significantly improve permanence and reduce undesirable weight losses

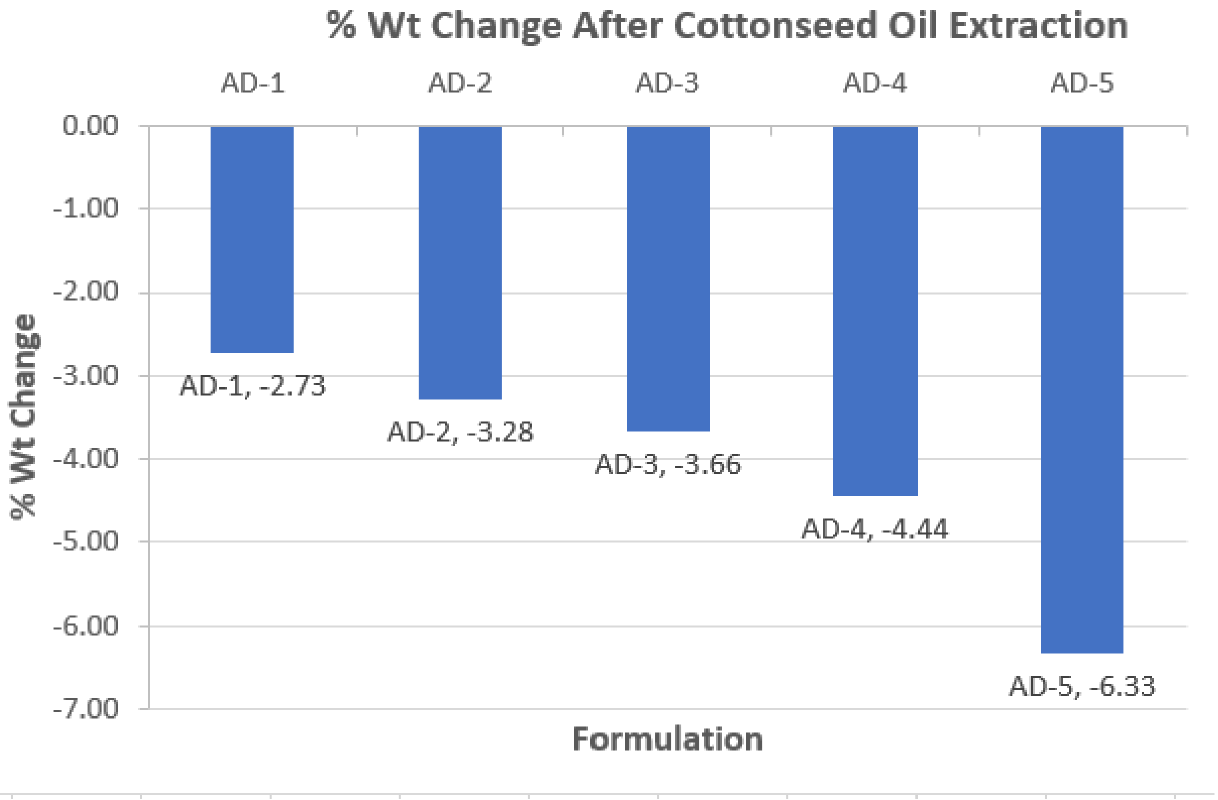
DI Water Extraction Data



Formulation	AD-1	AD-2	AD-3	AD-4	AD-5
% Polymeric Adipate	100	75	50	25	0
% Weight Change (Aged)	37.18	31.85	26.38	22.18	20.34
% Weight Change (Dry Out)	-1.0	-0.8	-0.6	-0.5	-0.4

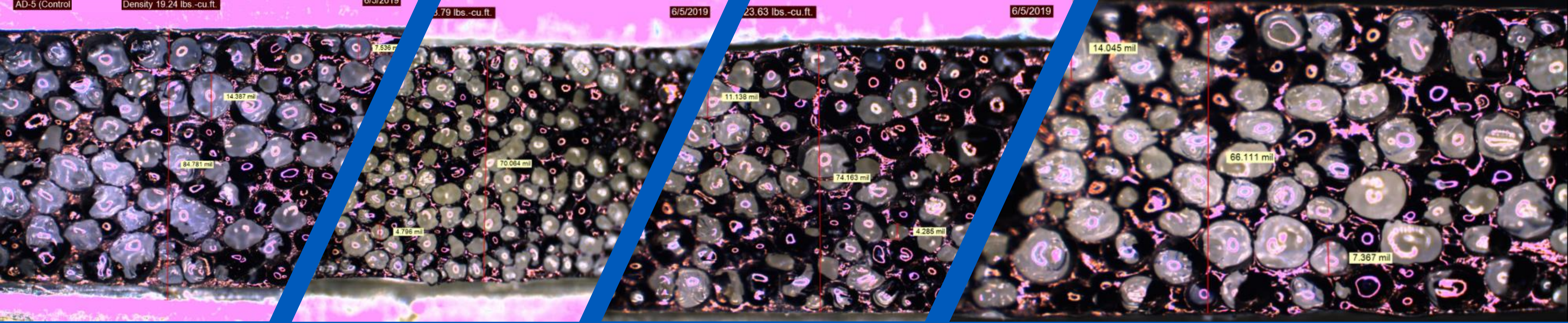
- Weight change after DI water aging and dry out show higher water-swell with increased level of polymeric adipate and slightly higher extraction after dry out
- These results clearly indicate that the increased polarity of polymeric adipate versus DIDP gives the vinyl foam product overall increased compatibility with highly polar solvents

Cottonseed Oil Extraction Data



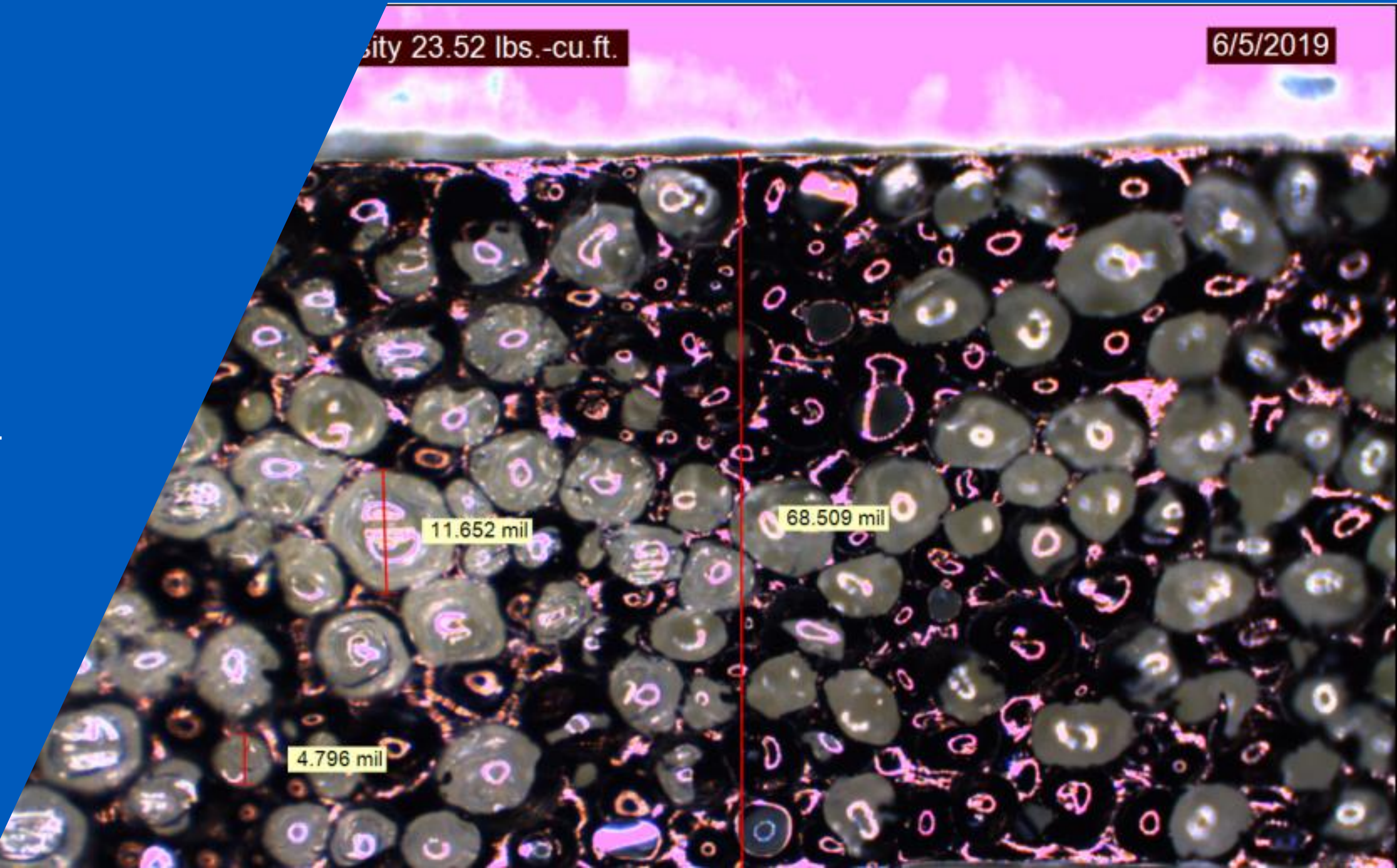
Formulation	AD-1	AD-2	AD-3	AD-4	AD-5
% Polymeric Adipate	100	75	50	25	0
% Weight Change	-2.73	-3.28	-3.66	-4.44	-6.33

- Weight loss after cottonseed oil extraction significantly decreases with increasing concentration of polymeric adipate in total plasticizer
- Results mirror behavior demonstrated in hexane solvent showing less extraction of the more polar, large polymeric adipate molecule and much more extraction of the low polarity DIDP in low polarity oil

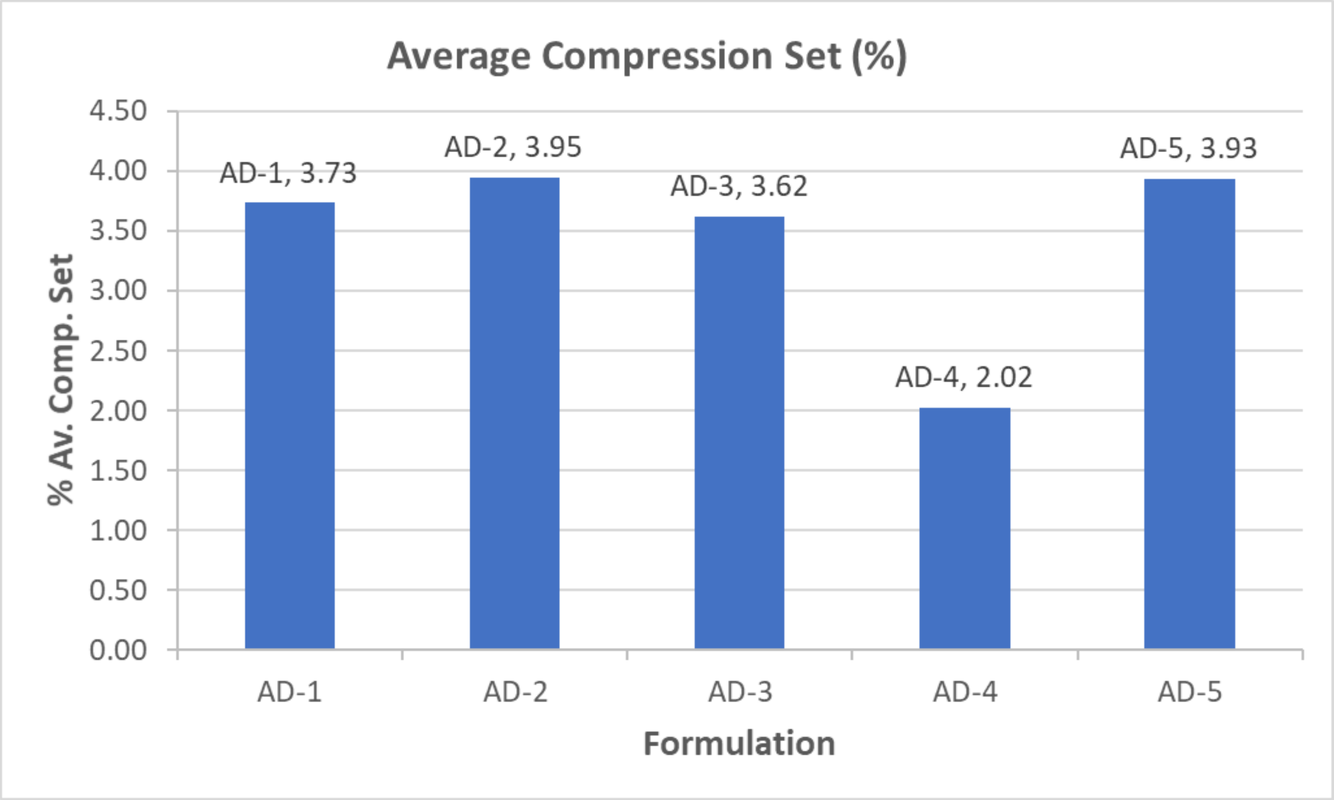


Microscopy Analysis

- Microscopic analysis indicates that all 5 samples exhibited similar cell size, uniformity and distribution throughout the foam specimens
- Foam thicknesses of AD-1, AD-2, AD-3, AD-4 and AD-5 samples were 70.046, 68.509, 74.163, 66.111 and 84.781 mils respectively
- The level of polymeric adipate in the vinyl foam seems to have little effect on the size, uniformity and distribution of foam cells



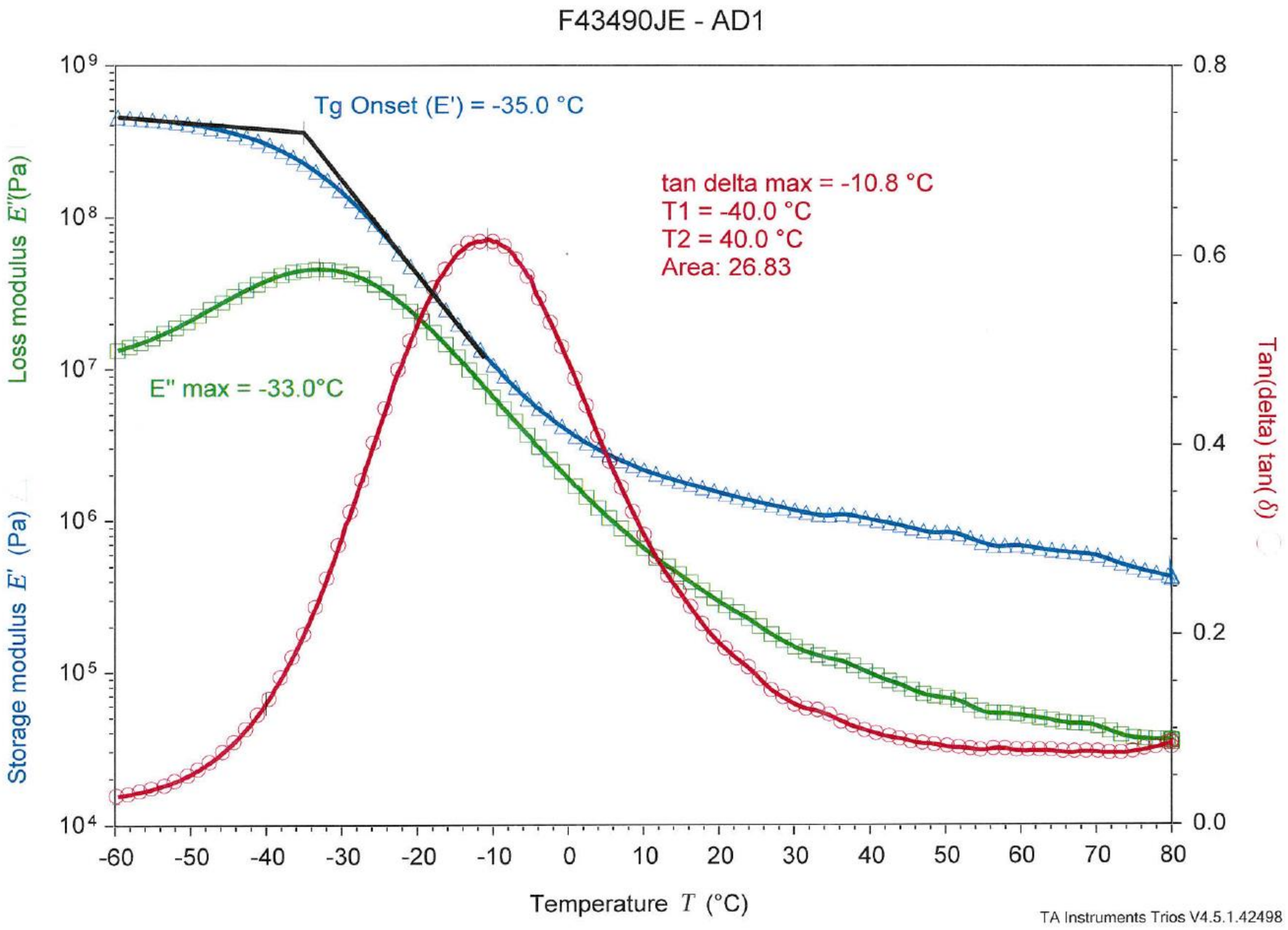
Compression Set Analysis



Formulation	AD-1	AD-2	AD-3	AD-4	AD-5
% Polymeric Adipate	100	75	50	25	0
Average Compression Set (%)	3.73	3.95	3.62	2.02	3.93

- Compression Set was measured using ASTM D 1056
  - 22h under 25% compression at RT
  - rest for 24h at RT after releasing compression
  - measure thickness after relaxation, and
  - calculate compression set from the initial thickness
- Results indicate that partial replacement of DIDP with polymeric adipate improves initial compression set by almost 50%
- Higher levels of polymeric adipate do not lead to further improvement of compression set performance

DMA Analysis



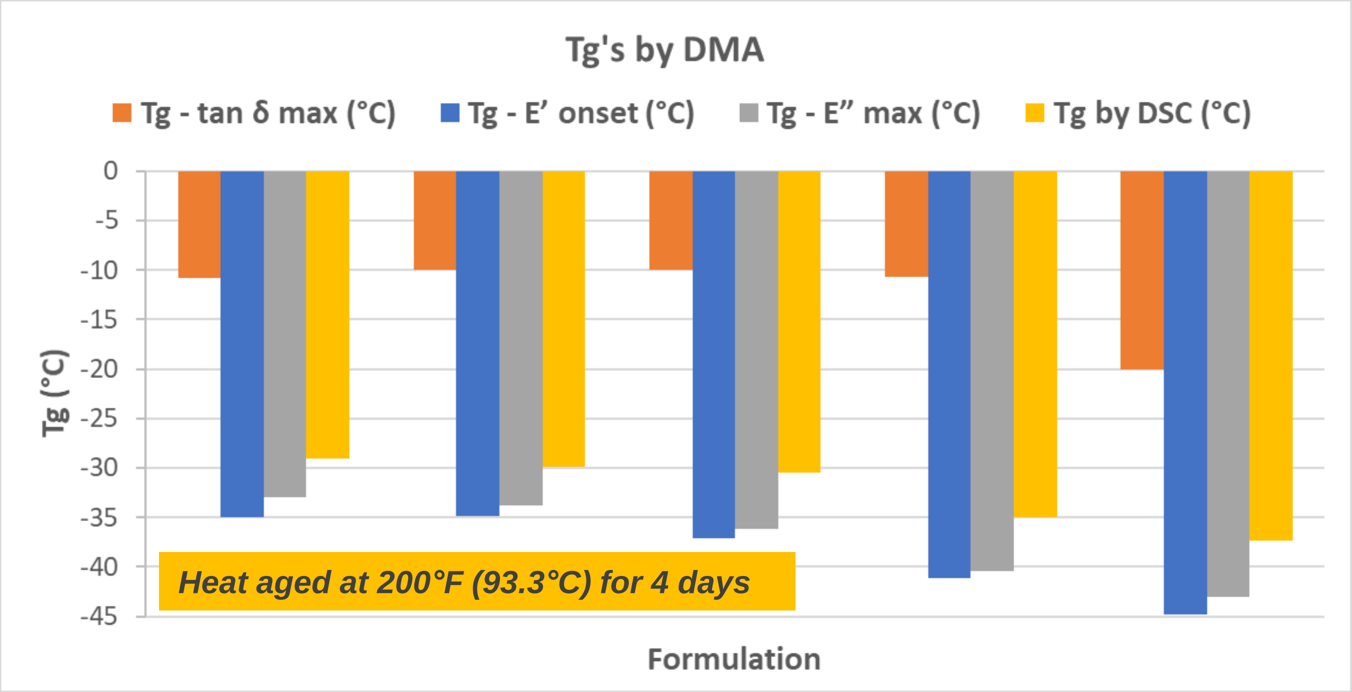
DMA Method Parameters

- Mode: Tensile
- Temperature Range: -60 °C to +80°C
- Strain: 0.5%
- Frequency: 1 Hz

DMA Analysis

Sample ID	AD1	AD1 Heat Aged	AD2	AD2 Heat Aged	AD3	AD3 Heat Aged	AD4	AD4 Heat Aged
Tg - tan δ max (°C)	-10.8	-4.7	-10	-4.8	-10	-5.2	-10.7	-6.5
Tg - E’ onset (°C)	-35	-32.1	-34.8	-29.9	-37.1	-32.7	-41.1	-37.8
Tg - E” max (°C)	-33	-27.3	-33.8	-28.1	-36.1	-31.4	-40.4	-37.2
Area Under tan δ Curve (-40°C to 40°C)	26.83	27.66	26.33	27.72	25.65	27.05	24.31	26.69
Elastic Modulus [x10^6] @ -40°C (Pa)	301.9	354.34	297.75	369.07	303.98	317.54	246.57	259.44
Elastic Modulus [x10^6] @ 0°C (Pa)	3.91	6.3	4.72	7.61	5.77	6.91	6.74	6.52
Elastic Modulus [x10^6] @ 25°C (Pa)	1.33	1.43	1.46	1.65	1.74	1.54	2.06	1.62
Loss Modulus [x10^6] @ -40°C (Pa)	38.5	27.27	42.05	32.49	49.49	37.13	52.23	45.54
Loss Modulus [x10^6] @ 0°C (Pa)	1.9	3.73	2.27	4.47	2.62	3.72	2.67	3.08
Loss Modulus [x10^6] @ 25°C (Pa)	0.21	0.31	0.23	0.36	0.28	0.33	0.35	0.34

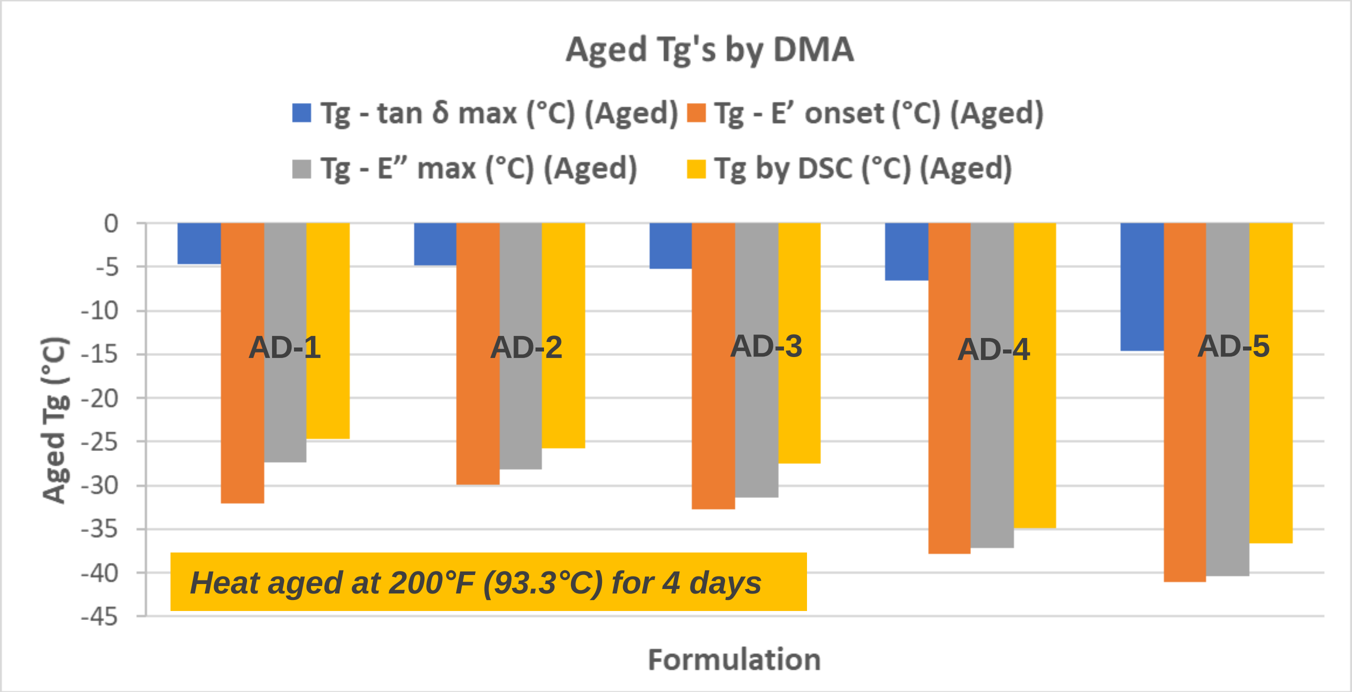
Glass Transitions Before Ageing (DMA Data)



Formulation	AD-1	AD-2	AD-3	AD-4	AD-5
% Polymeric Adipate	**100**	**75**	**50**	**25**	**0**
Tg by DSC (°C)	-29.03	-29.82	-30.48	-34.99	-37.34
Tg - tan δ max (°C)	-10.8	-10.0	-10.0	-10.7	-20.1
Tg - E' onset (°C)	-35.0	-34.8	-37.1	-41.1	-44.8
Tg - E" max (°C)	-33.0	-33.8	-36.1	-40.4	-43.0

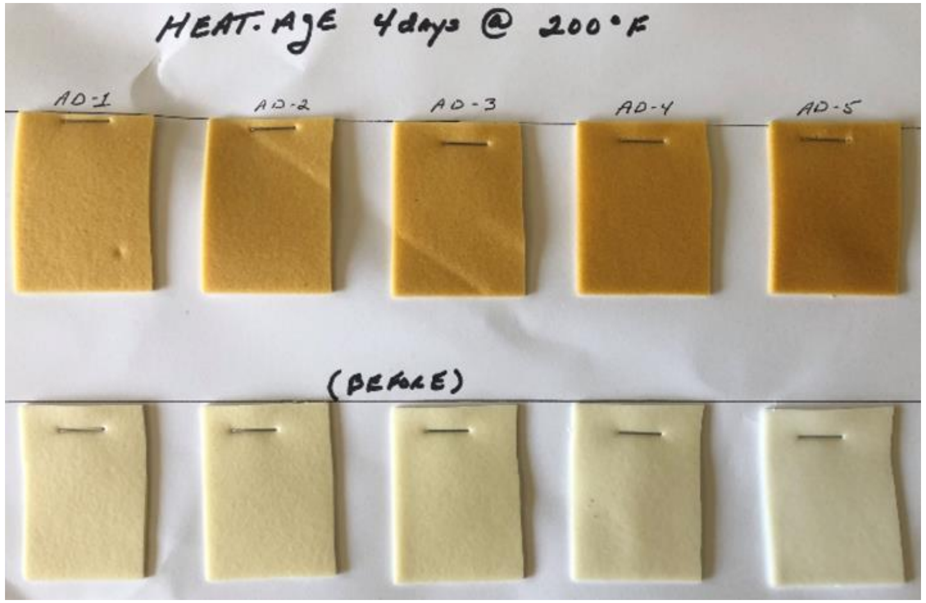
- DSC glass transition data correlate more closely with DMA data for E' onset and E" max than with tan δ max data
- Regardless of which Tg data one relies on, the difference between glass transitions for pure DIDA (AD-5) and pure polymeric adipate (AD-1) is always around 10°C
- While the E' onset and E" max data show gradual decrease with increasing concentration of polymeric adipate, the tan δ max data show consistent Tg's regardless of the polymeric adipate concentration

Glass Transitions After Heat Ageing (DMA Data)

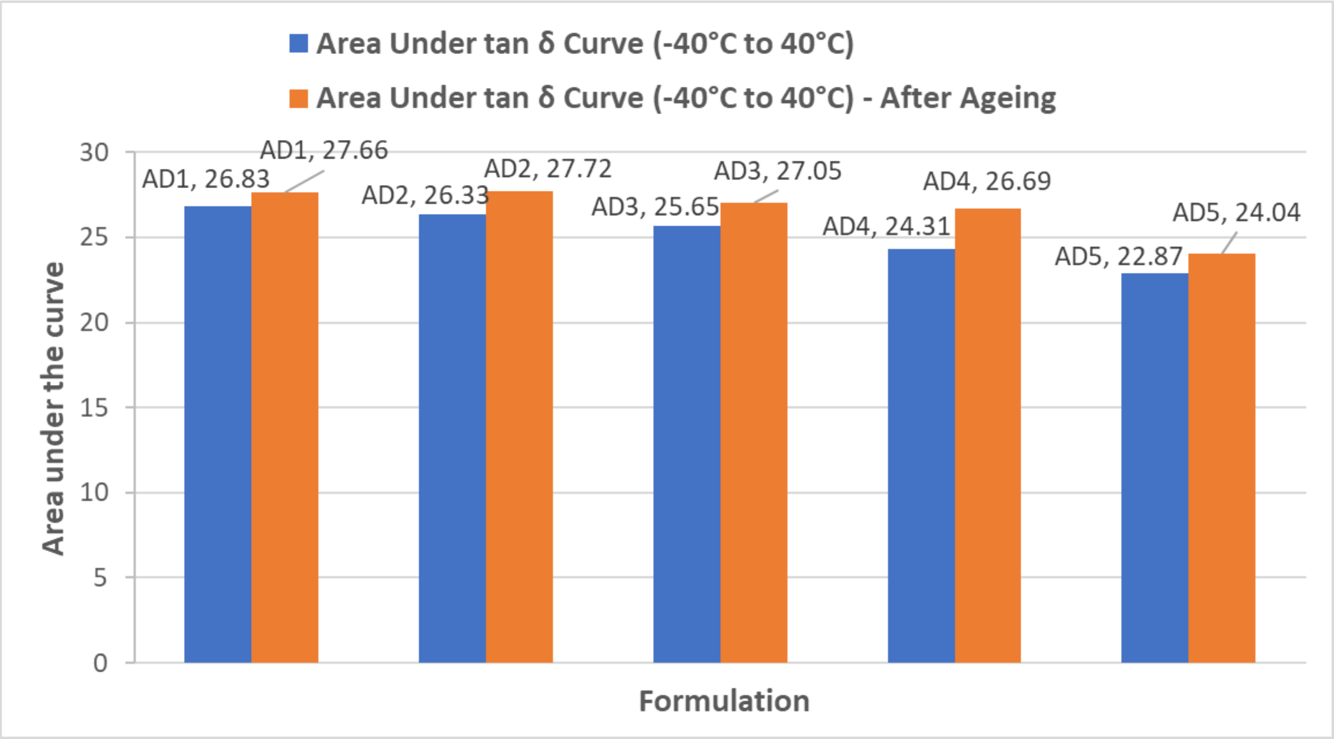


Formulation	AD-1	AD-2	AD-3	AD-4	AD-5
% Polymeric Adipate	**100**	**75**	**50**	**25**	**0**
Tg by DSC (°C) (Aged)	-24.66	-25.71	-27.53	-34.88	-36.67
Tg - tan δ max (°C) (Aged)	-4.7	-4.8	-5.2	-6.5	-14.6
Tg - E’ onset (°C) (Aged)	-32.1	-29.9	-32.7	-37.8	-41.1
Tg - E” max (°C) (Aged)	-27.3	-28.1	-31.4	-37.2	-40.4

- DSC glass transition data after ageing also correlate more closely with DMA data for E’ onset and E” max after ageing than with tan δ max data after ageing



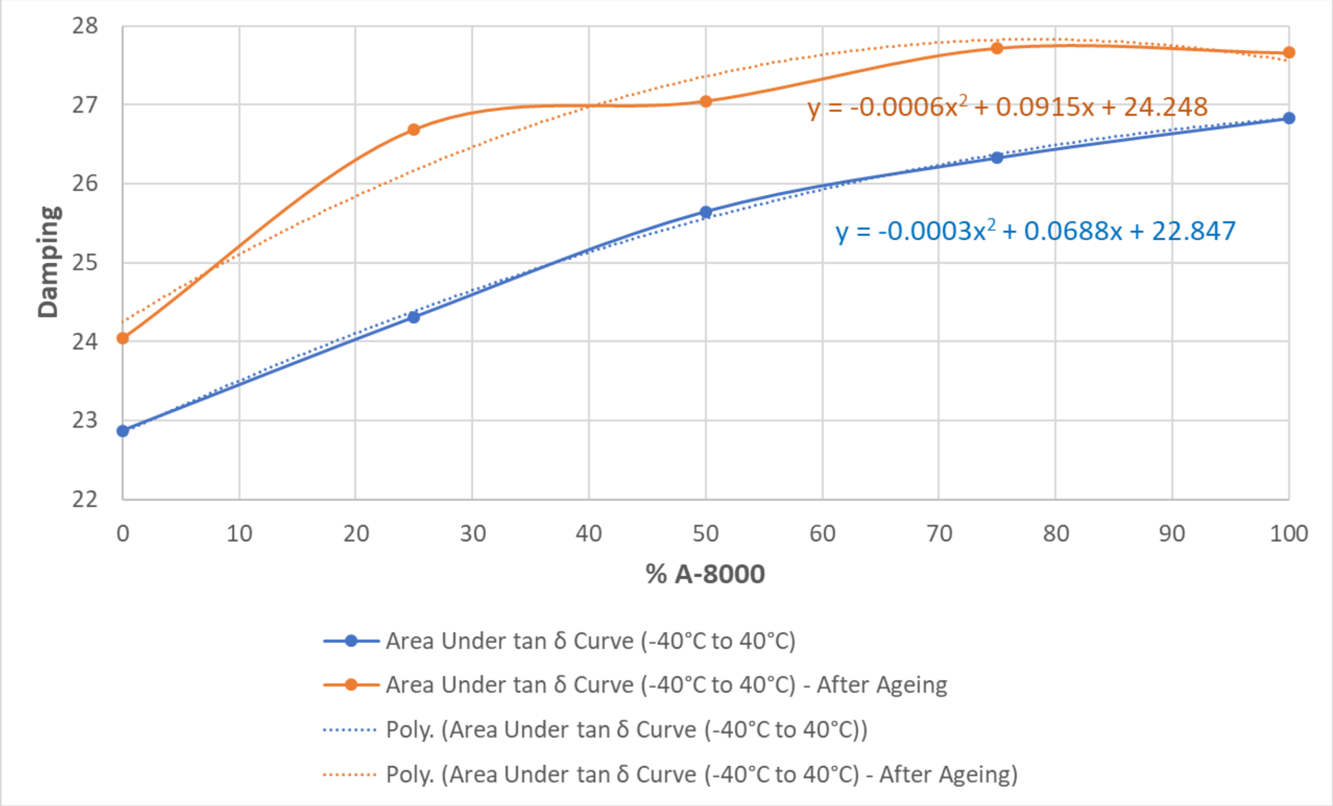
DMA Analysis – Damping Capabilities



Formulation	AD-1	AD-2	AD-3	AD-4	AD-5
% Polymeric Adipate	100	75	50	25	0
Area Under tan δ Curve (-40°C to 40°C)	26.83	26.33	25.65	24.31	22.87
Area Under tan δ Curve (-40°C to 40°C) - After Ageing	27.66	27.72	27.05	26.69	24.04

- DMA evaluates stiffness and damping, which are reported and modulus and tan delta values.
- E’ or Storage Modulus (in-phase component) and E” or Loss Modulus (out-of-phase component) measure samples elastic behavior
- The ratio of the E’/E” is called tan delta, aka Damping Factor, which measures energy of dissipation of the material

DMA Analysis – Damping Capabilities



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Area Under tan δ Curve (-40°C to 40°C) - After Ageing	27.66	27.72	27.05	26.69	24.04

- Increasing concentration of polymeric adipate modifier in the total plasticizer increases materials ability to dissipate energy in the -40 to +40°C temperature range (e.g. dampening of sound or vibrations)
- Complete replacement of DIDP (AD-5) with polymeric adipate modifier (AD-1) results in about 17% improvement in damping capacity
- This improvement is also maintained after heat ageing

CONCLUSIONS

Conclusions

- Vinyl foam of excellent quality can be produced using polymeric adipate plasticizer as both partial and full replacement for monomeric plasticizers
- Increasing concentration of polymeric plasticizer reduces shear-thinning behavior of resulting plastisol, which may be important for dipping or coating applications focused on filling cavities and gaps in the substrate
- Increased polymeric adipate concentration in the total plasticizer increases % Elongation progressively from 370% (100% monomeric) to about 450% (100% polymeric)
- Increasing polymeric adipate concentration in the total plasticizer results in gradual increase in Tg of the vinyl foam material due to lower plasticizing efficiency of polymeric adipate versus monomeric plasticizer
- Weight loss after hexane extraction drastically decreases with increasing concentration of polymeric adipate in total plasticizer. In fact, even small levels of polymeric adipate significantly improve hexane resistance

Conclusions

- Microscopic analysis indicates that all samples exhibited similar cell size and distribution throughout the foam specimens. The level of polymeric adipate in the vinyl foam seems to have little effect on the size and distribution of foam cells
- Results indicate that partial replacement of DIDA with polymeric adipate improves initial compression set by almost 50%. Higher levels of polymeric adipate do not lead to further improvement of compression set performance
- DSC glass transition data correlate more closely with DMA data for E’ onset and E” max than with tan δ max data
- Increasing concentration of polymeric adipate modifier in the total plasticizer increases materials ability to dissipate energy in the -40 to +40°C temperature range (e.g. dampening of sound or vibrations). Complete replacement of monomeric plasticizer with polymeric adipate results in about 17% improvement in damping capacity

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