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Investigation of Film Properties in Air-Curable Methyl-Modified and Methyl/Phenyl-Modified Silicone Resins Using Tetramethylguanidine and Tetrabutyl Titanate Catalysts

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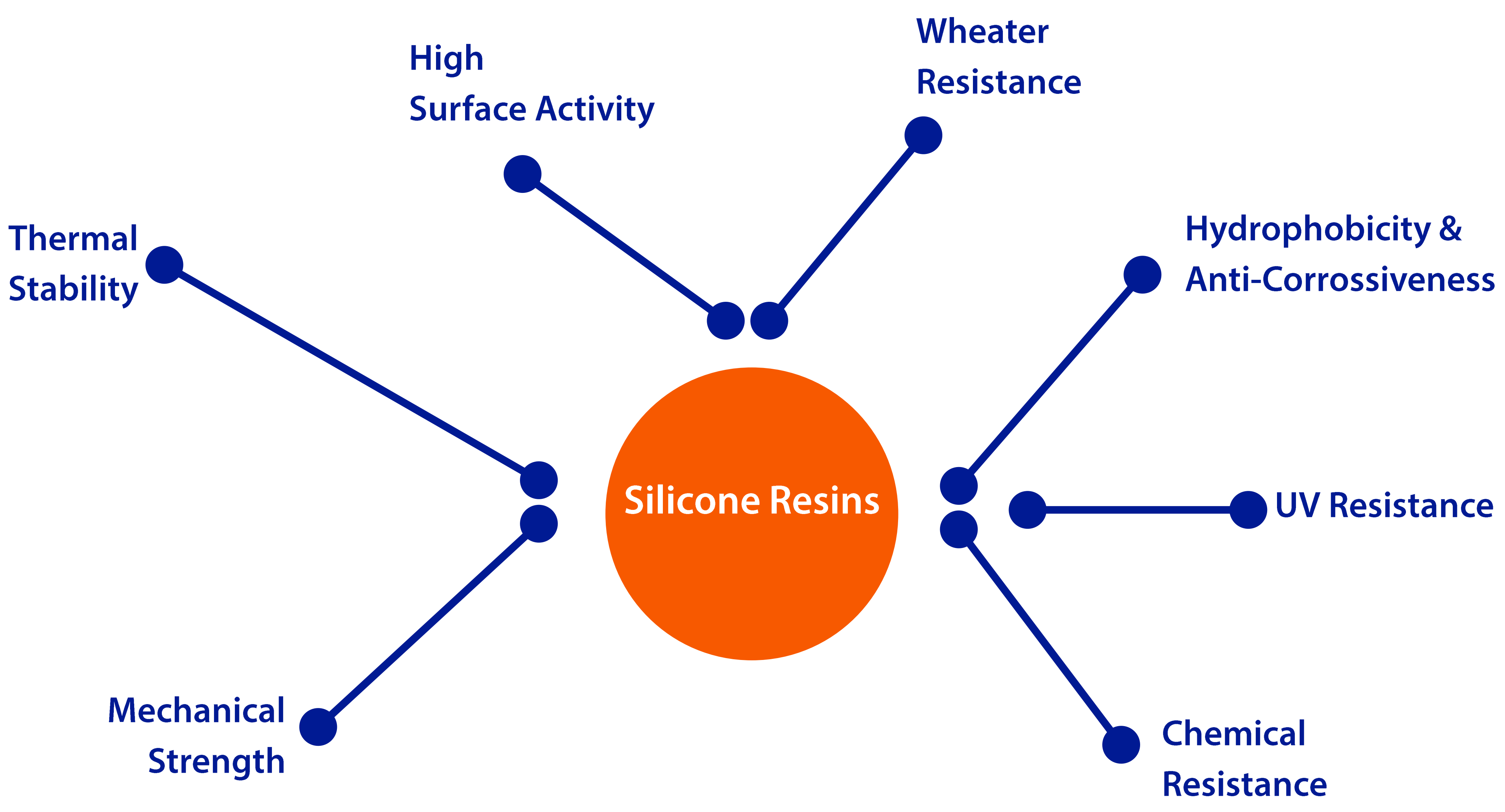
Denge Kimya

Silicone Resins in Coatings



"Silicone Resins play a crucial role in modern" protective Coatings

They are very suitable for heavy-duty applications

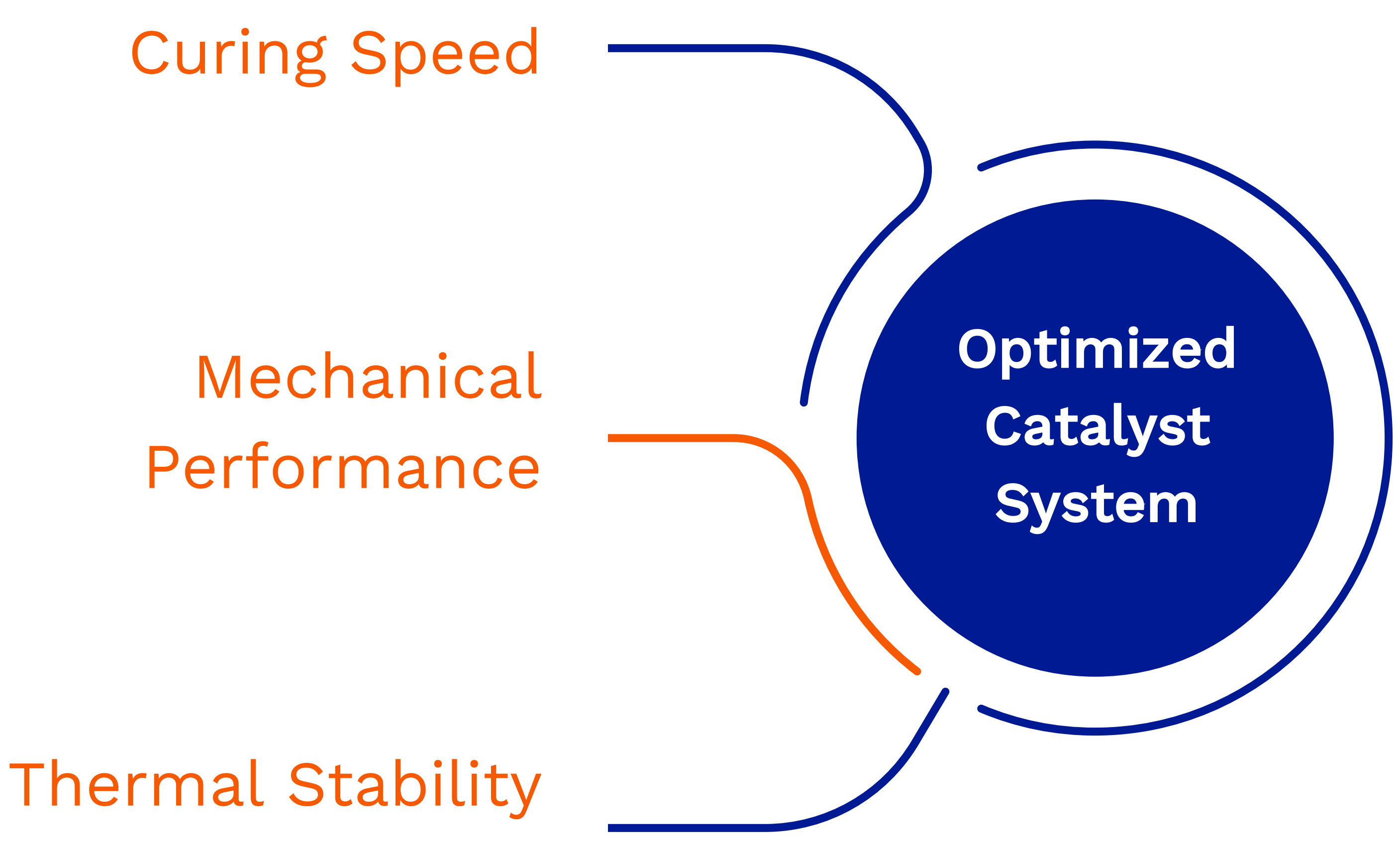
Types of Silicone Resins

Methyl-modified and methyl-phenyl-modified resins are widely applied.

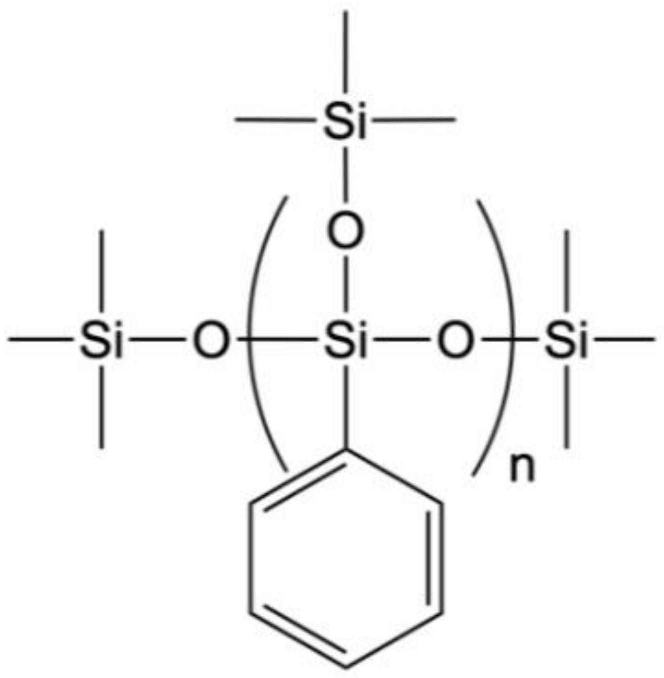
Methyl: better flexibility, basic weatherability
Methyl-phenyl: enhanced thermal resistance and mechanical strength

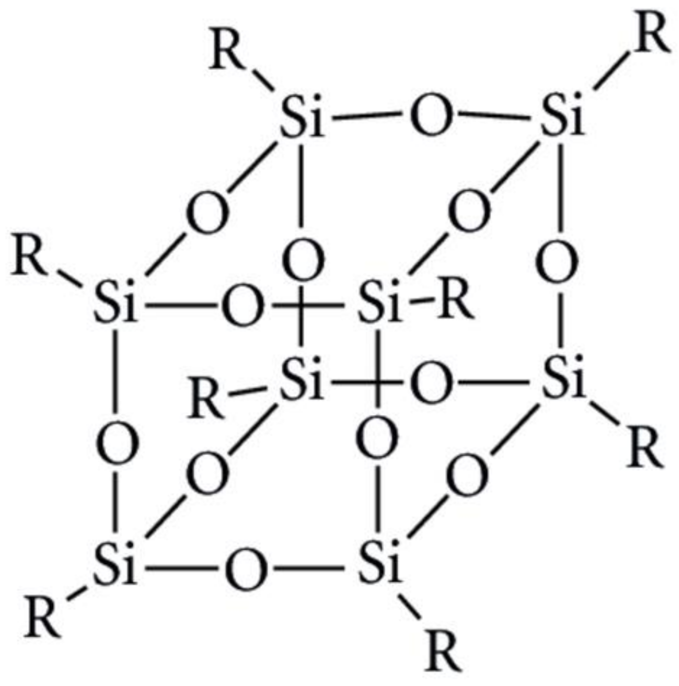
Air-Curable Systems

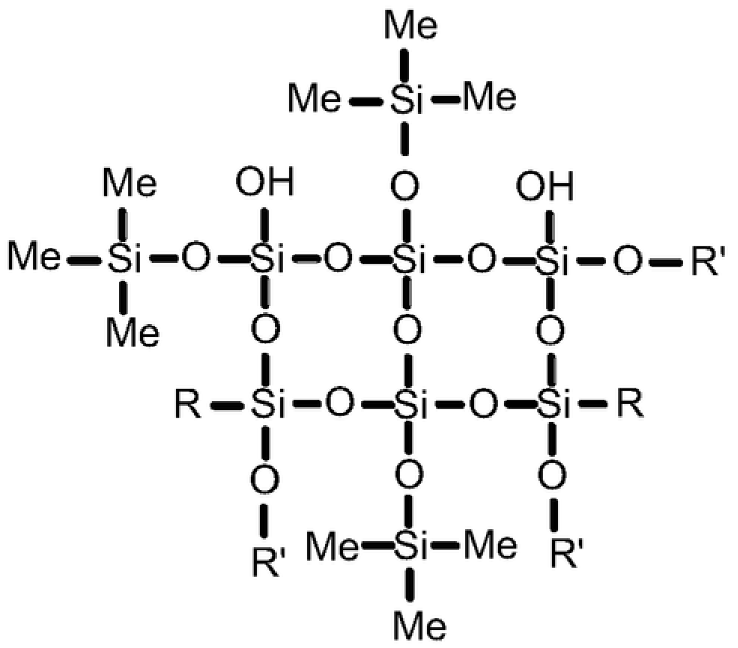
- Demand for ambient curing due to energy savings and process simplicity.
- Performance heavily influenced by catalyst selection.



"Silicone resins play a key role in modern protective coatings, especially where durability and environmental resistance are critical. In particular, methyl- and methyl-phenyl-modified resins are chosen based on the balance between flexibility, hardness, and thermal stability."

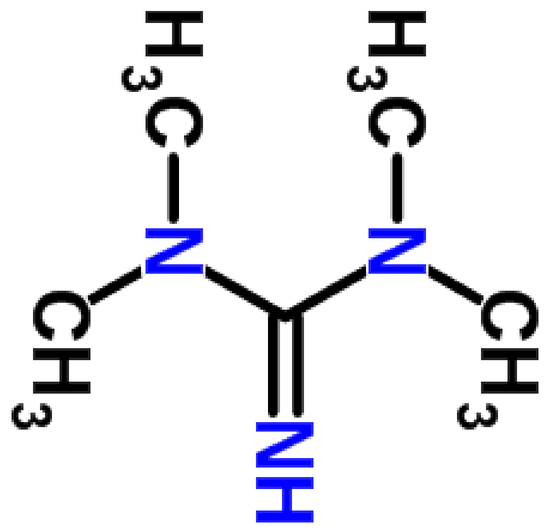






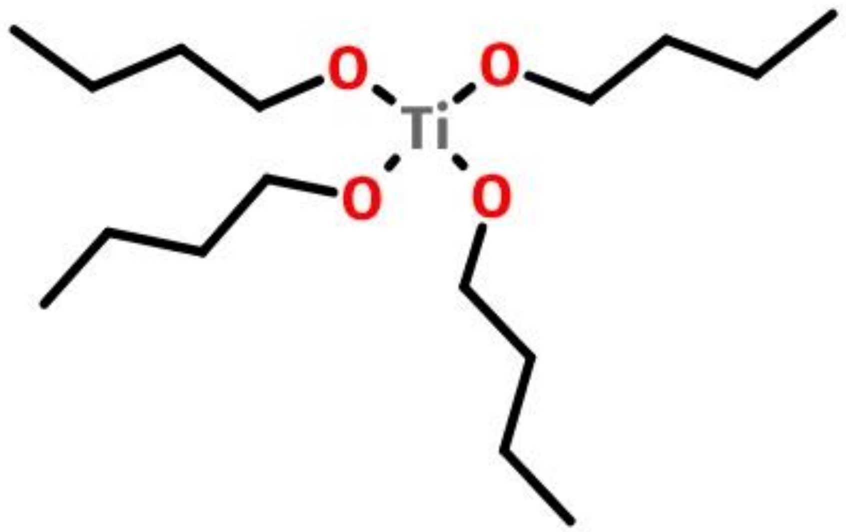
1. Tetramethylguanidine (TMG)

- Strong organic base catalyst
- Promotes rapid surface curing
- Results in high surface hardness
- Suitable for fast-drying coatings
- Limited in improving adhesion/flexibility



2. Tetrabutyl Titanate (TBT)

- Metal alkoxide catalyst
- Facilitates deeper crosslinking
- Enhances adhesion and flexibility
- Slower curing profile
- Sensitive to hydrolysis/moisture



1. Silicone Resin Types

Methyl-modified silicone resin
Methyl-phenyl-modified silicone resin

Chosen for their thermal durability and mechanical flexibility

2. Catalyst Systems Investigated

Pure **TMG**
Pure **TBT**
TBT modified with **acetylacetone (AcAc)**
Various AcAc:TBT ratios

Dual Catalyst Systems:
TMG + TBT combinations in different ratios

3. Formulation Variables

Resin-to-catalyst ratio kept constant
AcAc:TBT and TMG:TBT ratios systematically varied.

Coating applied by **draw-down** application, air-**cured under ambient conditions for 7 days.**

1. Film Formation & Curing

Coatings applied on **metal** substrates
Ambient air-curing over controlled time periods: **7 days**

Observed gel time and surface drying

2. Mechanical & Surface Tests

Hardness: Pencil hardness method (ASTM D3363 or similar)
Adhesion: Cross-cut test (ASTM D3359)
Gloss: Measured at 60° angle using glossmeter
Flexibility: Mandrel bend test (ASTM D522 or equivalent)

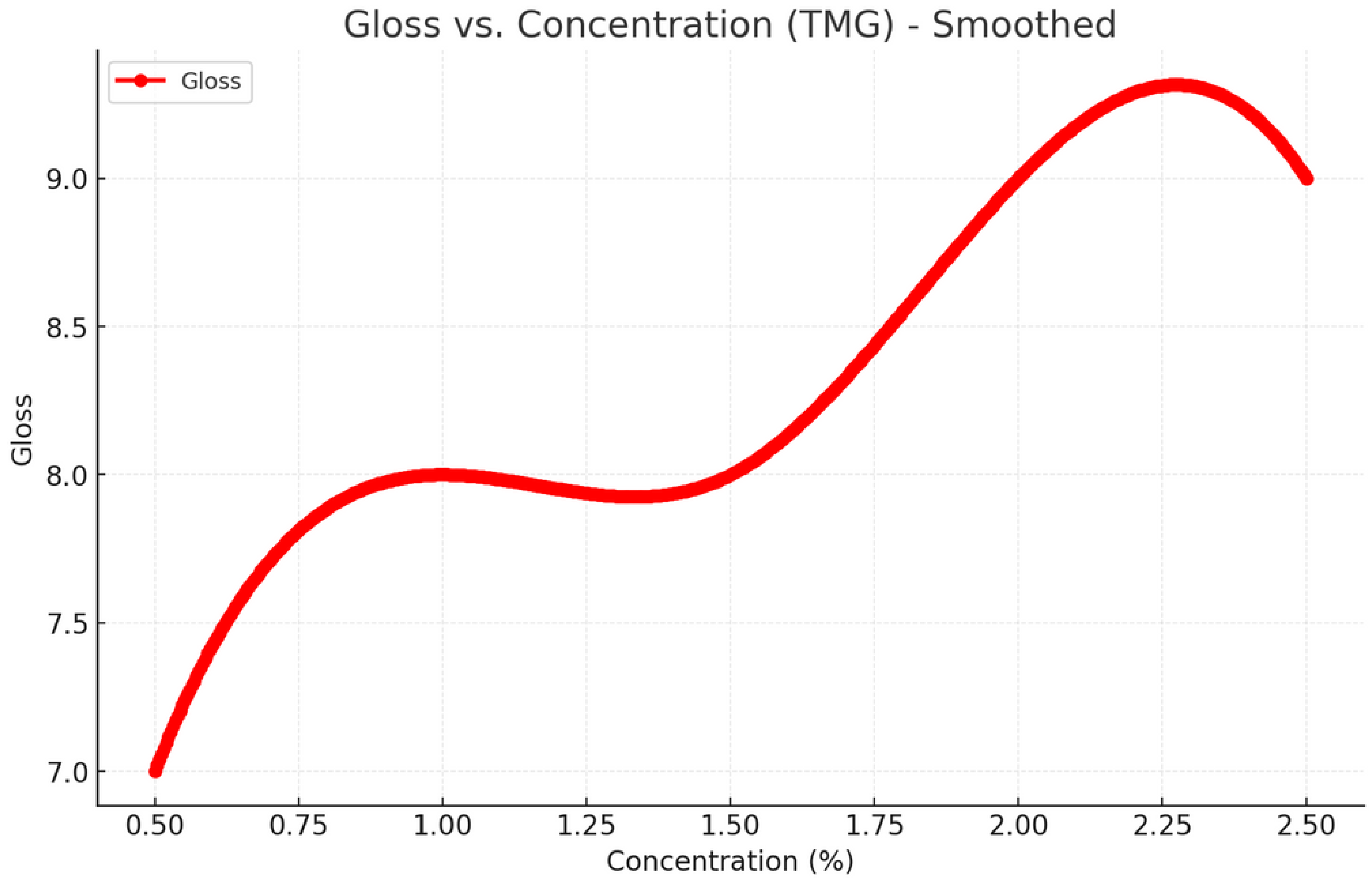
3. Thermal Characterization

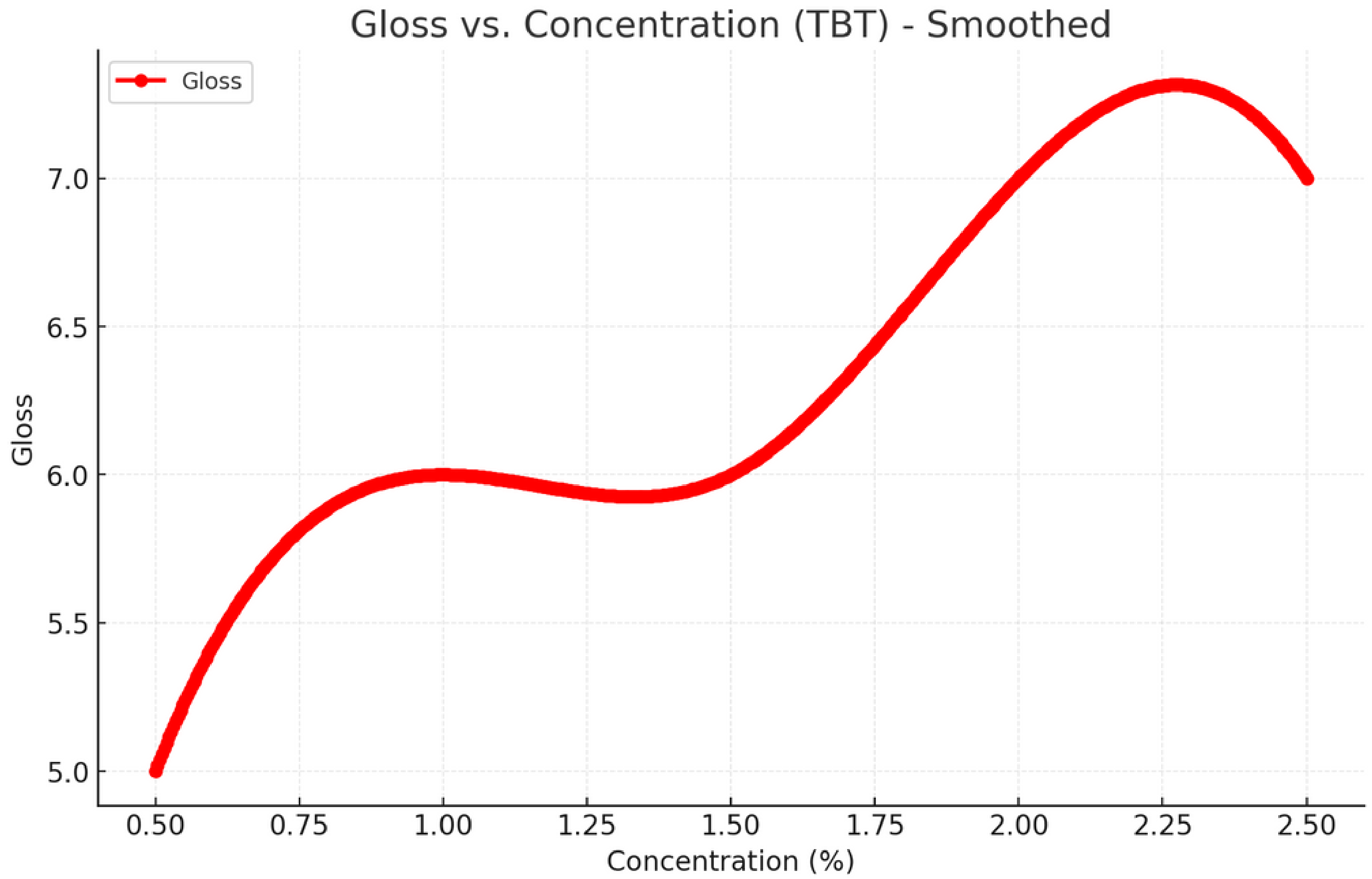
TGA (Thermogravimetric Analysis): thermal degradation profile
DSC (optional): crosslinking behavior or Tg shift

4. Cure Kinetics Observation

Visual & touch observation of gel time
Influence of catalyst type and ratio on cure speed

Effect of the catalyst on gloss properties





When we compare the gloss properties of the coating films cured with TBT and TMG, the change in profile with concentration difference looks familiar, but the gloss properties of TMG is better than the TBT cured films.

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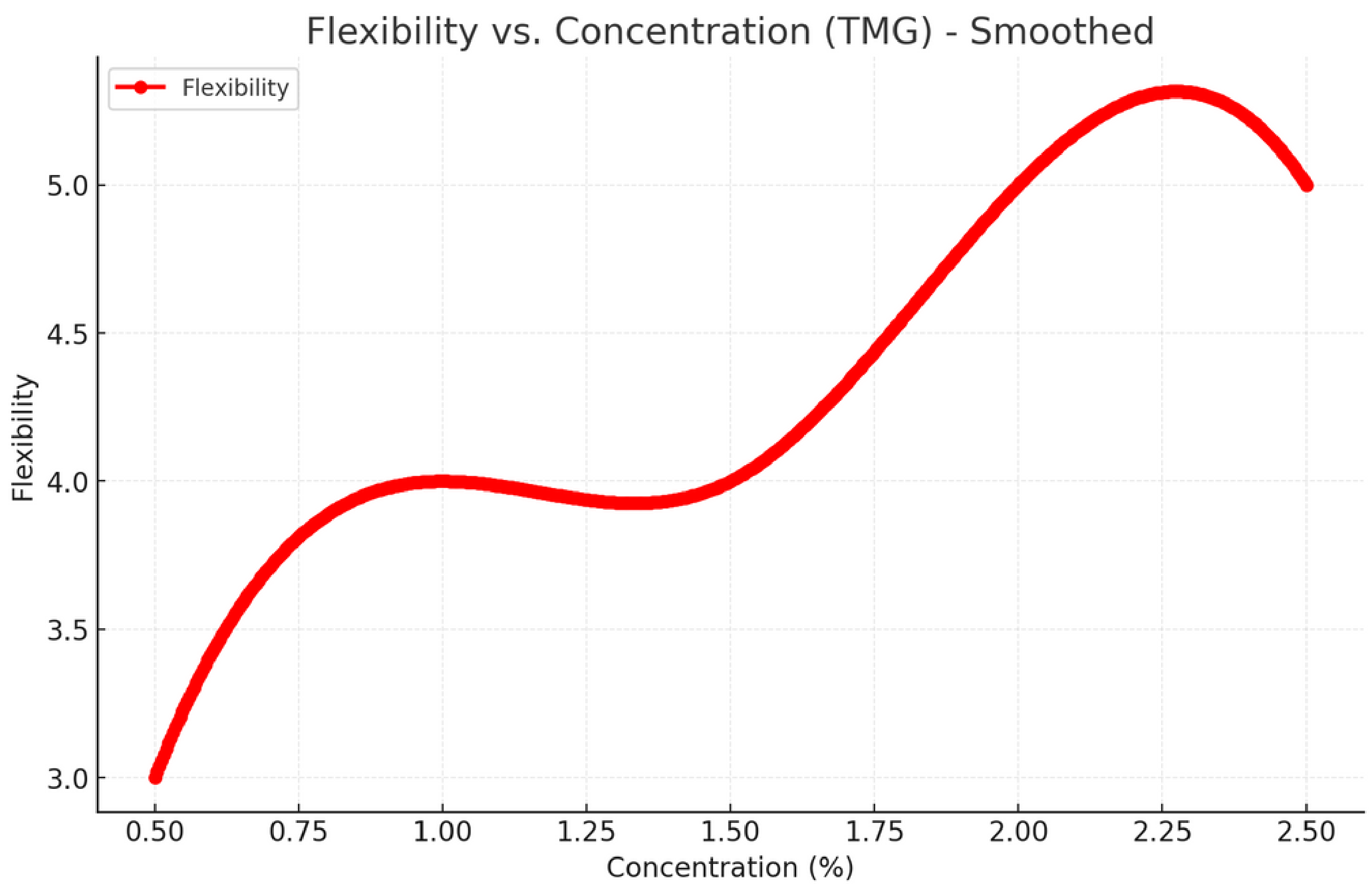
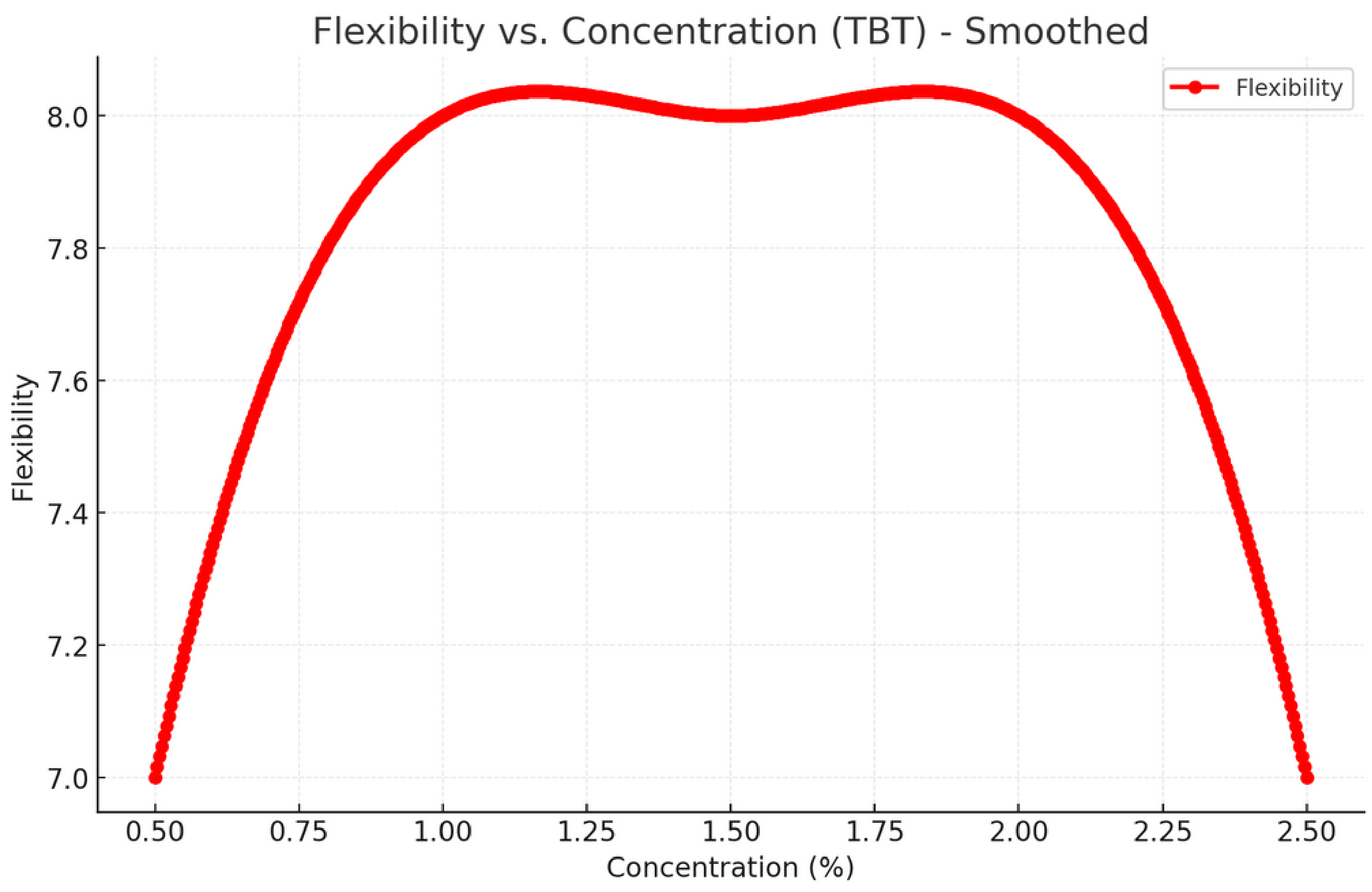
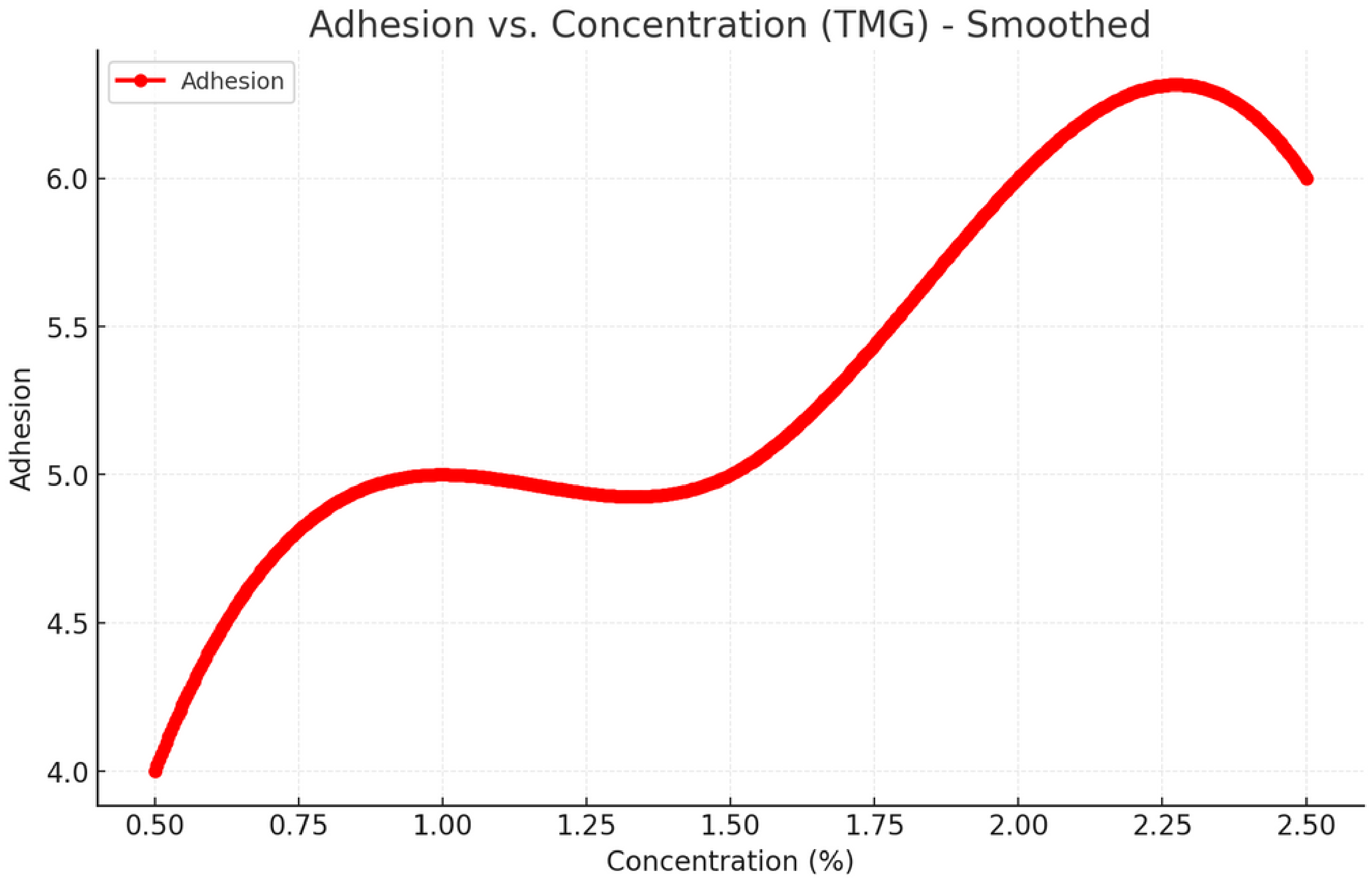
Effect of the catalyst on flexibility properties

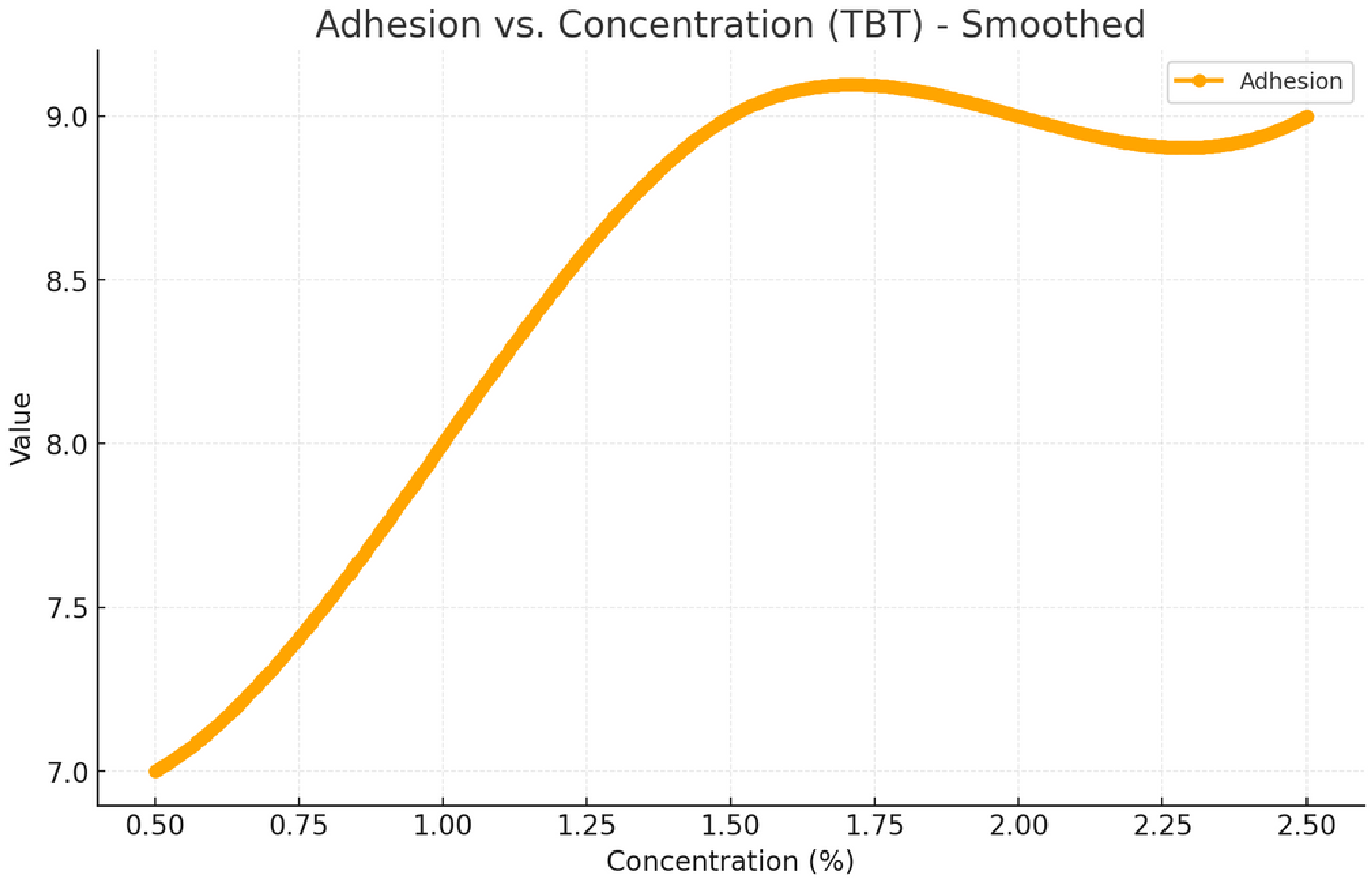




Flexibility is increasing up to 2% of the catalyst concentration. Higher dosages make the film more brittle. TMG increases the brittleness compared to the TBT.

Effect of the catalyst on adhesion properties





Adhesion requires TBT curing for ambient curable silicone resins. Increase in the concentration helpsadhesion but cross-linking degree increament causes loss in adhesion.

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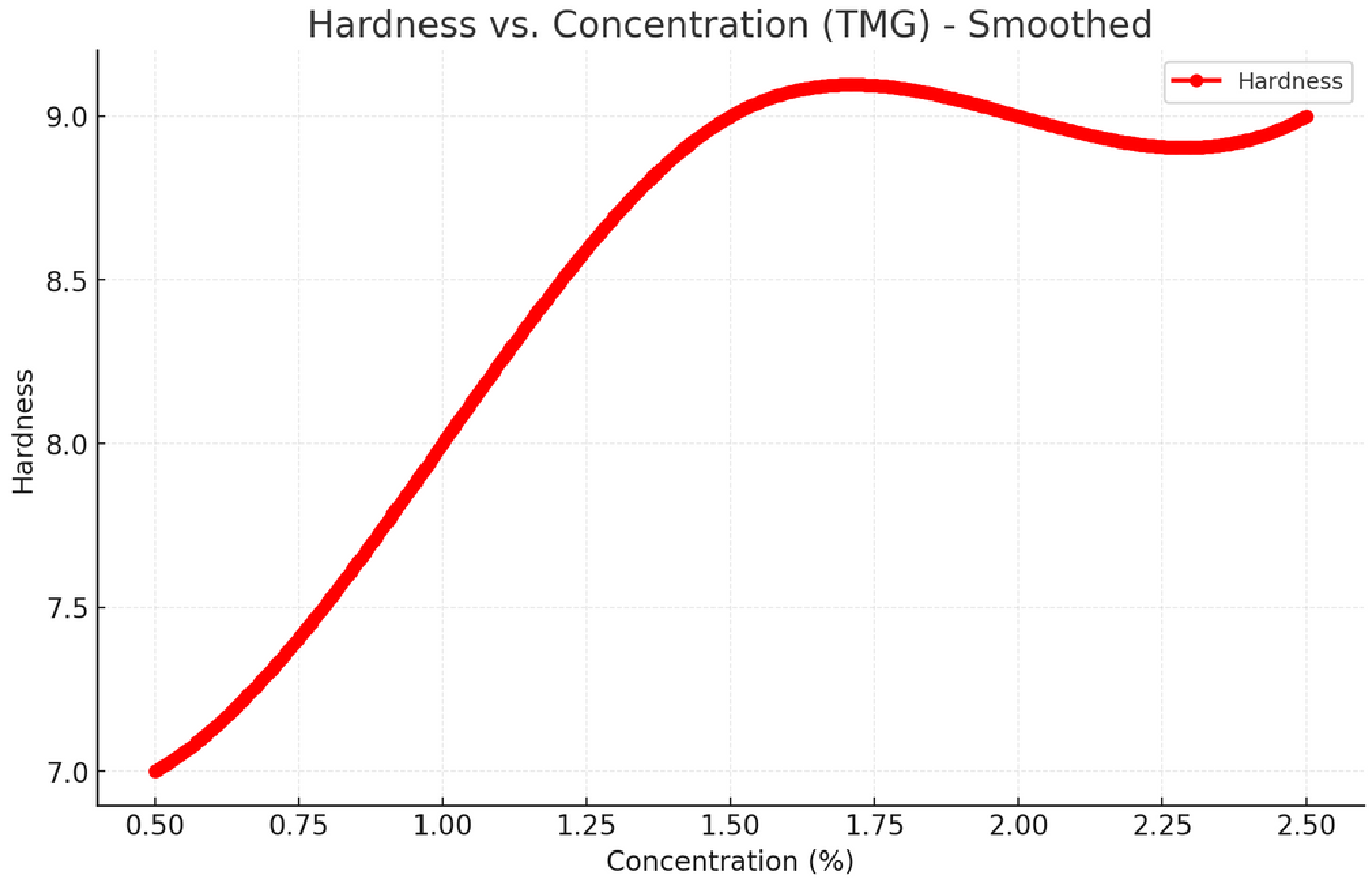
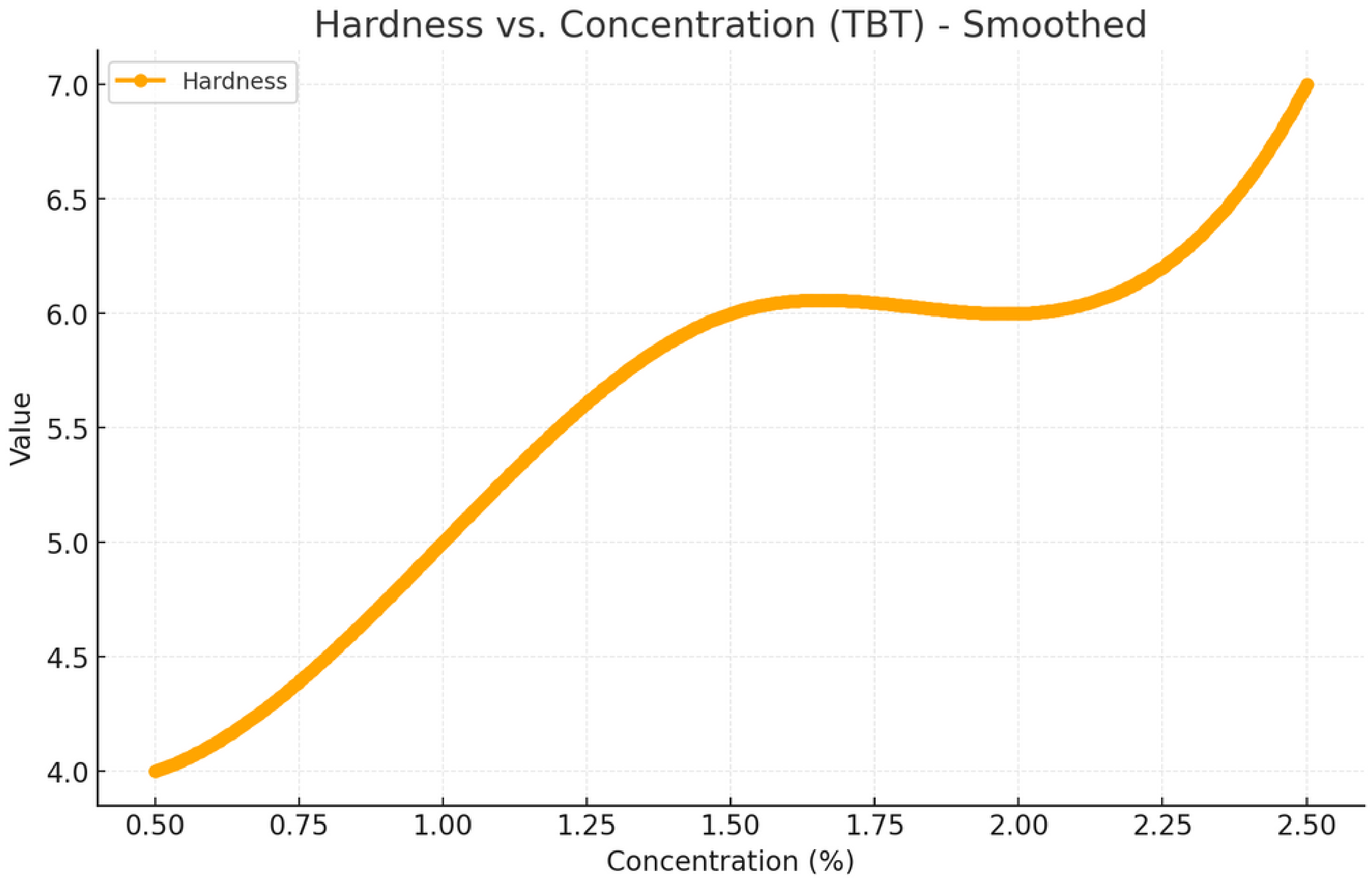
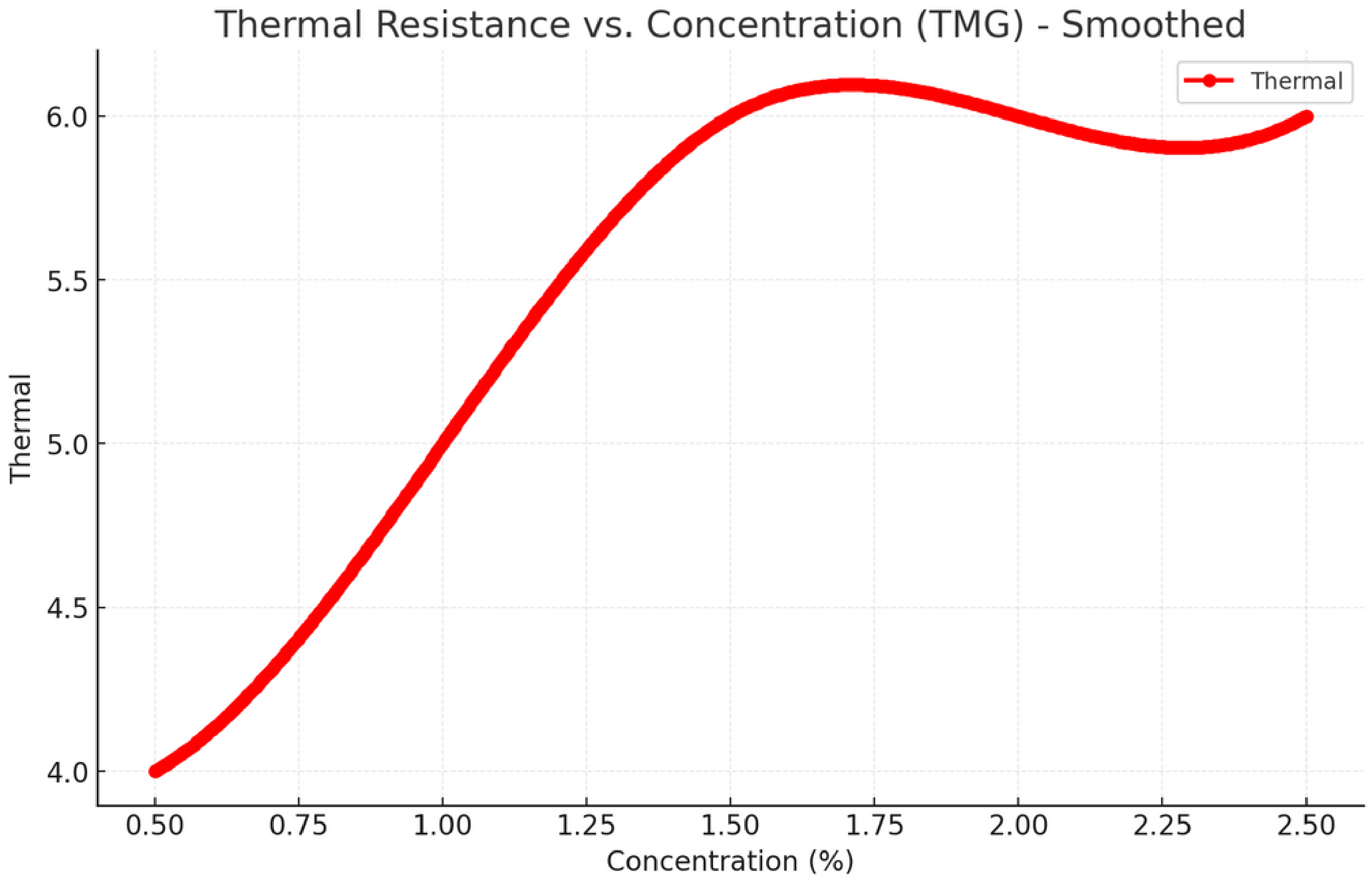
Effect of the catalyst on hardness properties

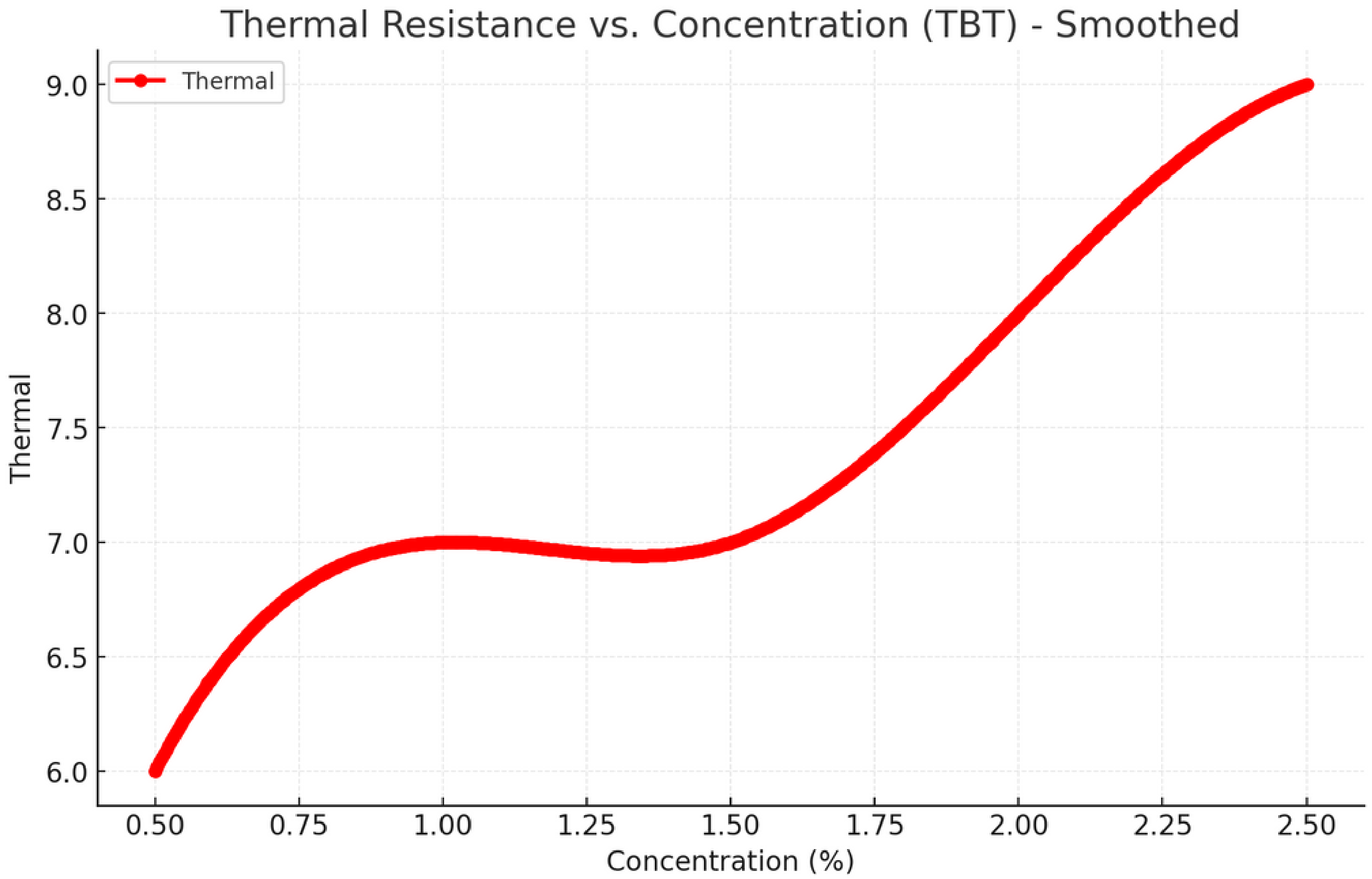




TMG improves the hardness of the film. Surface curing is very affected by curing with TMG. TBT can also increase hardness but requires high catalyst dosages.

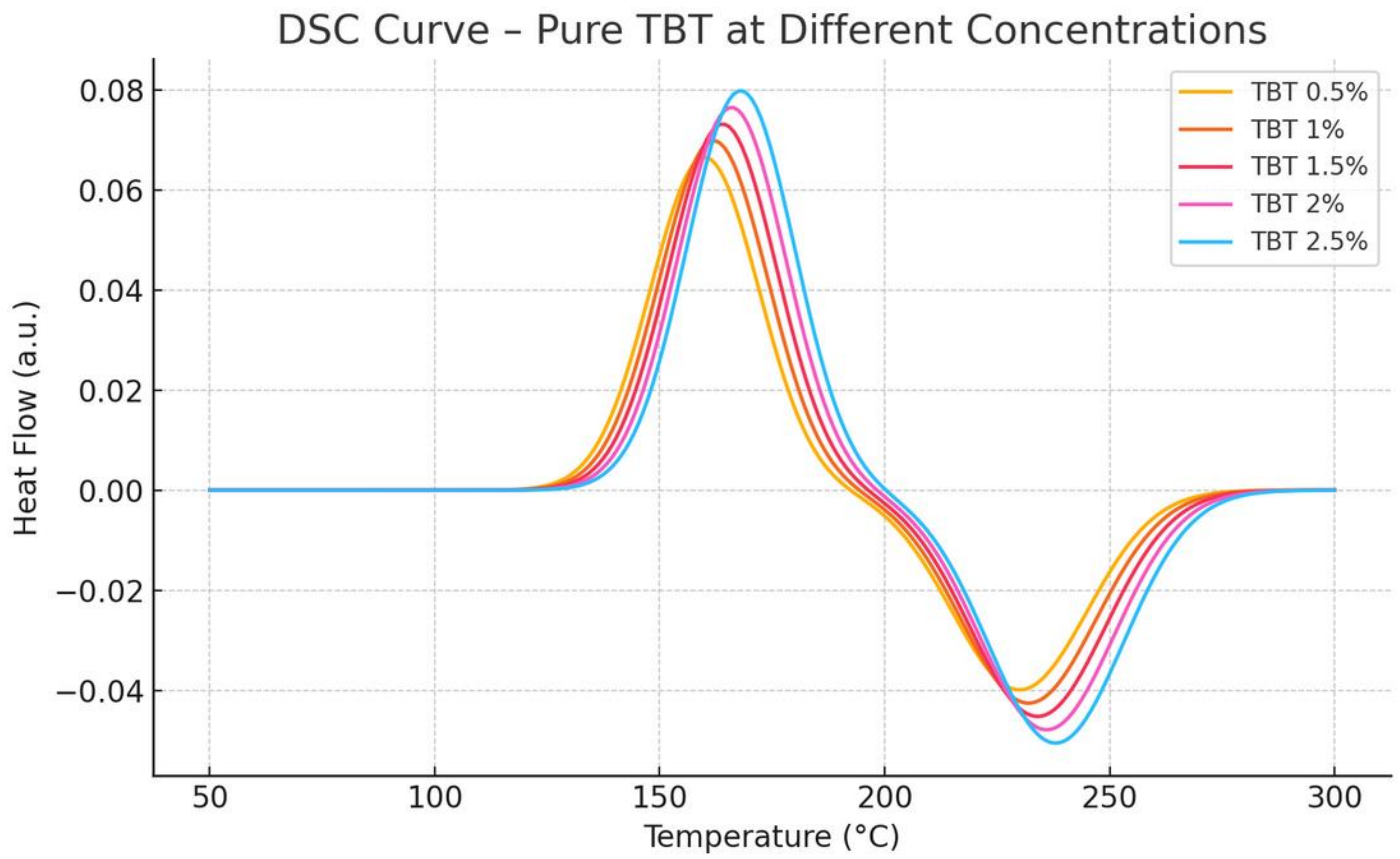
Effect of the catalyst on thermal properties

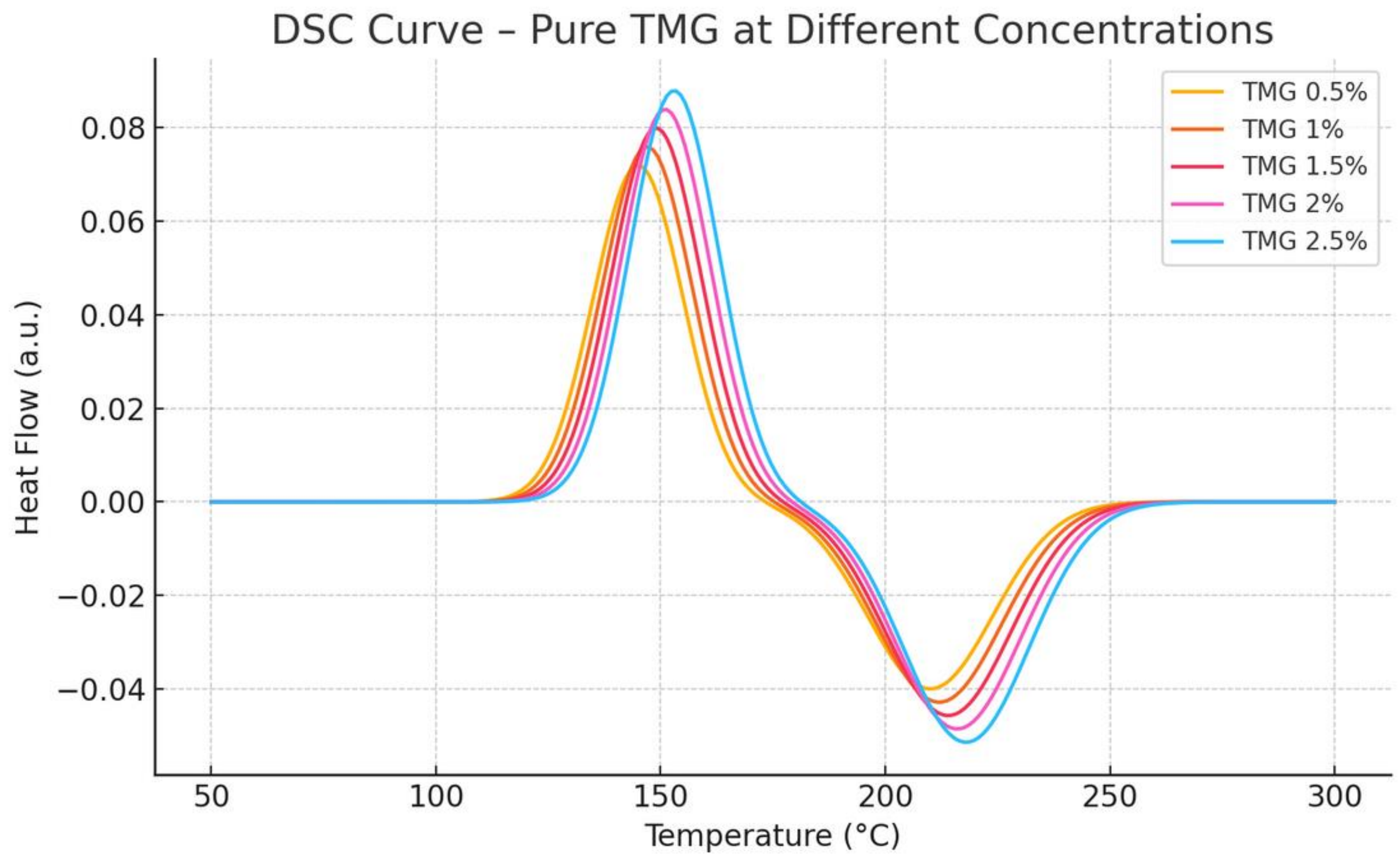




Thermal resistance increased with the TBT catalyst. TMG does not react with resins; however, TBT reacts with the resin and creates Ti-O-Si units which helps thermal stability.

Thermal Analysis Results - DSC





The Tg temperature differs from both the concentration and the catalyst type. An increase in concentration increases the Tg of the dry film. High concentration of the catalyst causes an increase in cross-linking at higher temperatures.

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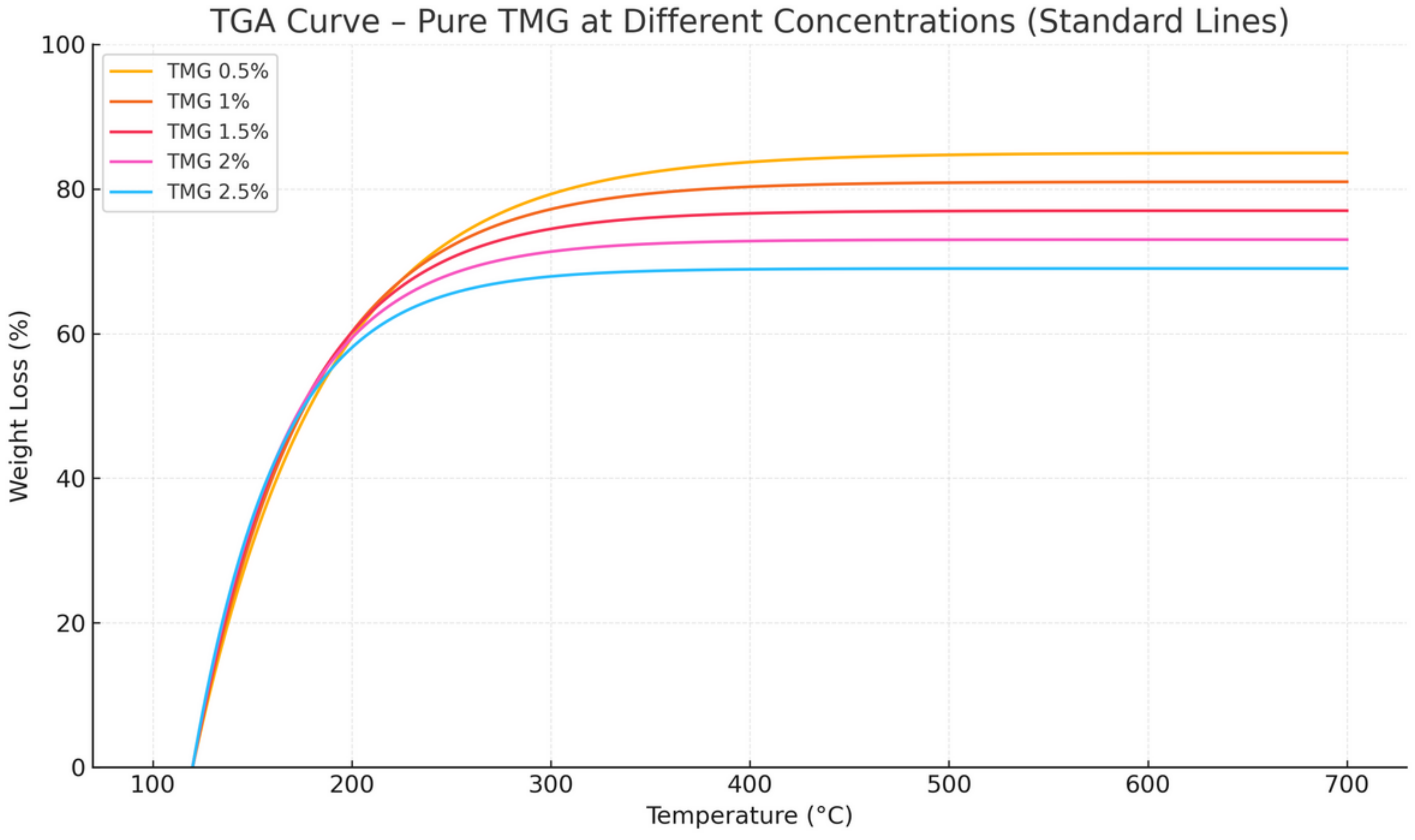
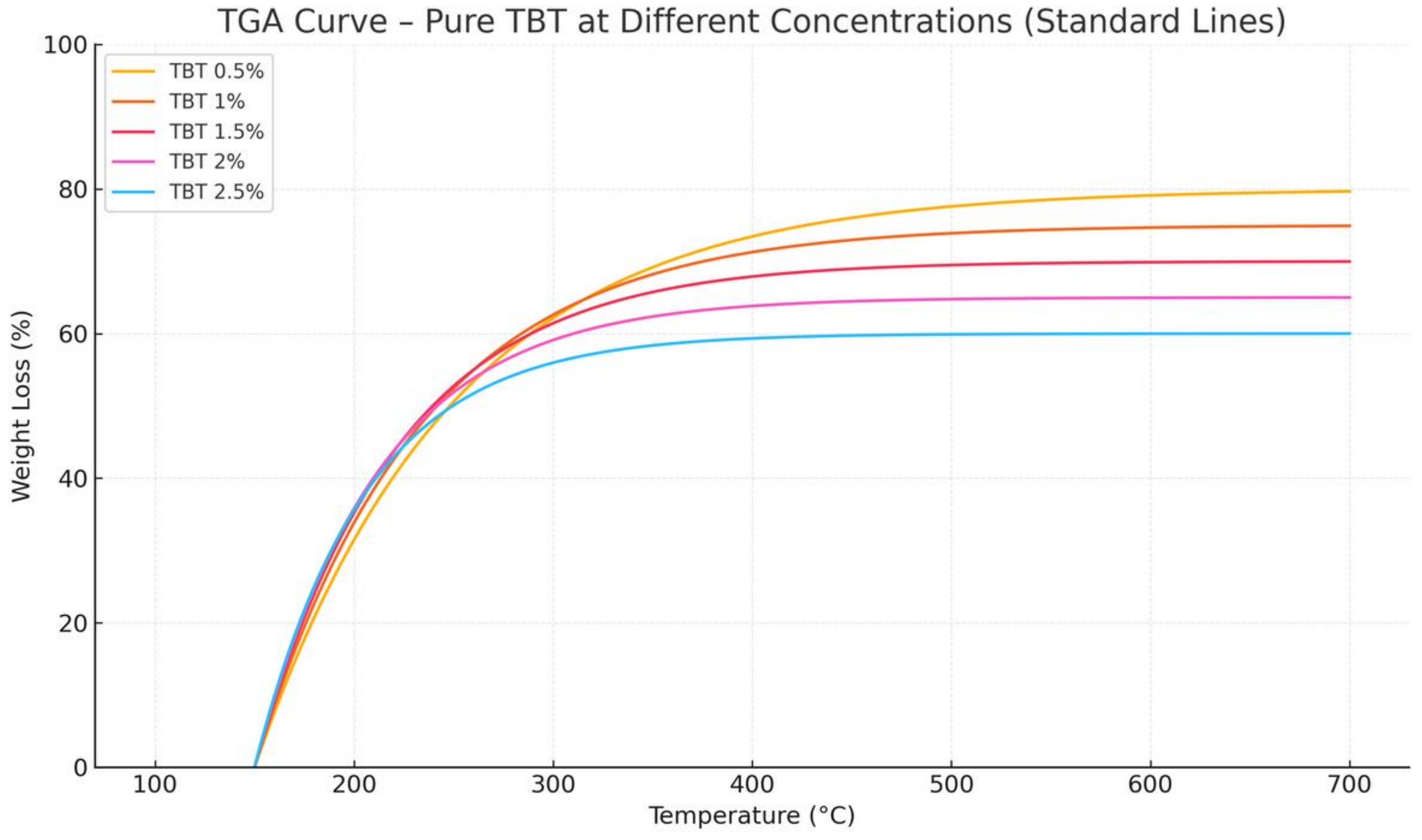
Thermal Analysis Results - TGA





With higher dosages, the cross-linking degree is higher, which gives lower weight loss in TGA analysis. TBT improves thermal stability. Degradation starts at higher temperatures with TBT curing.

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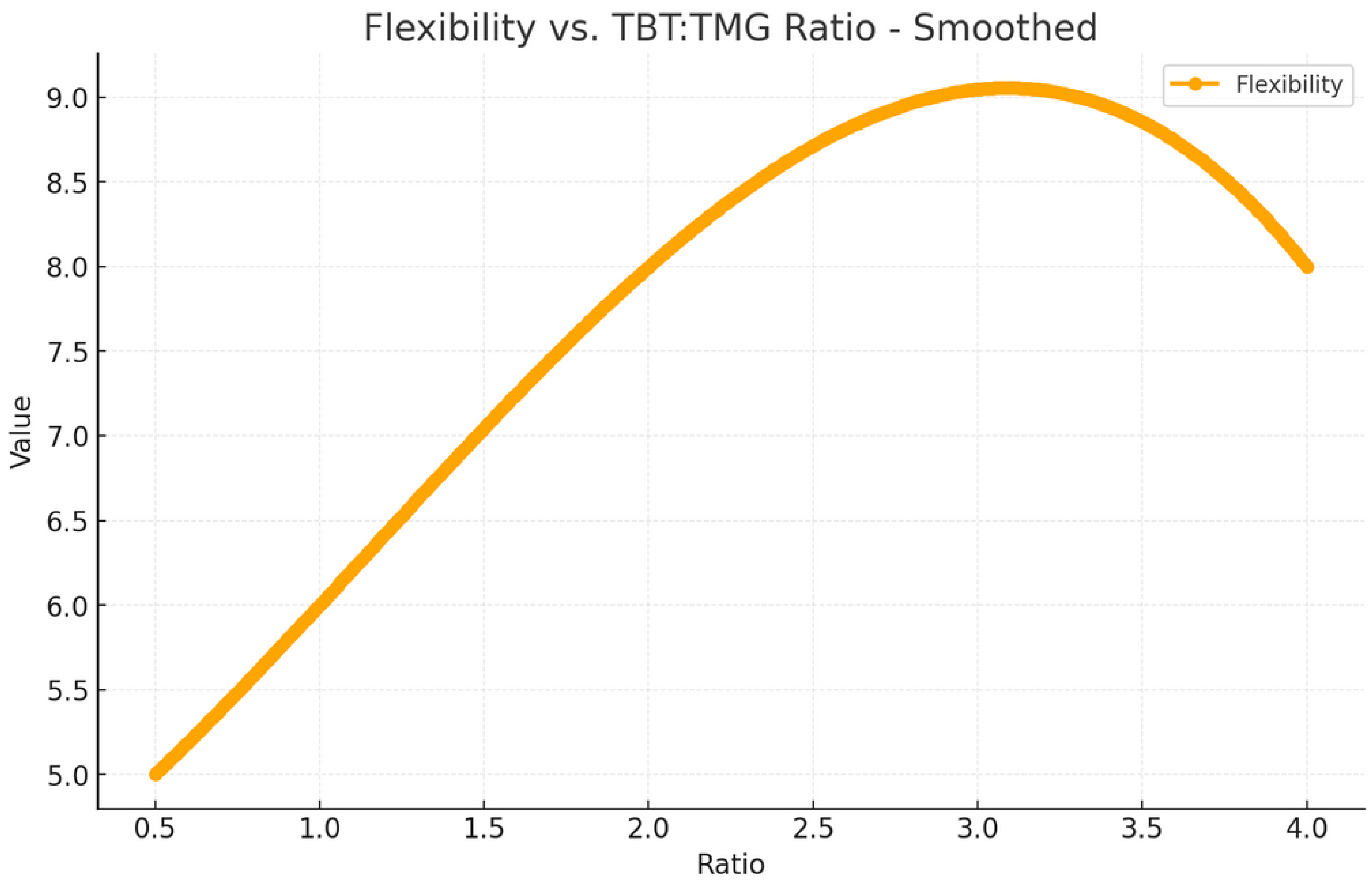
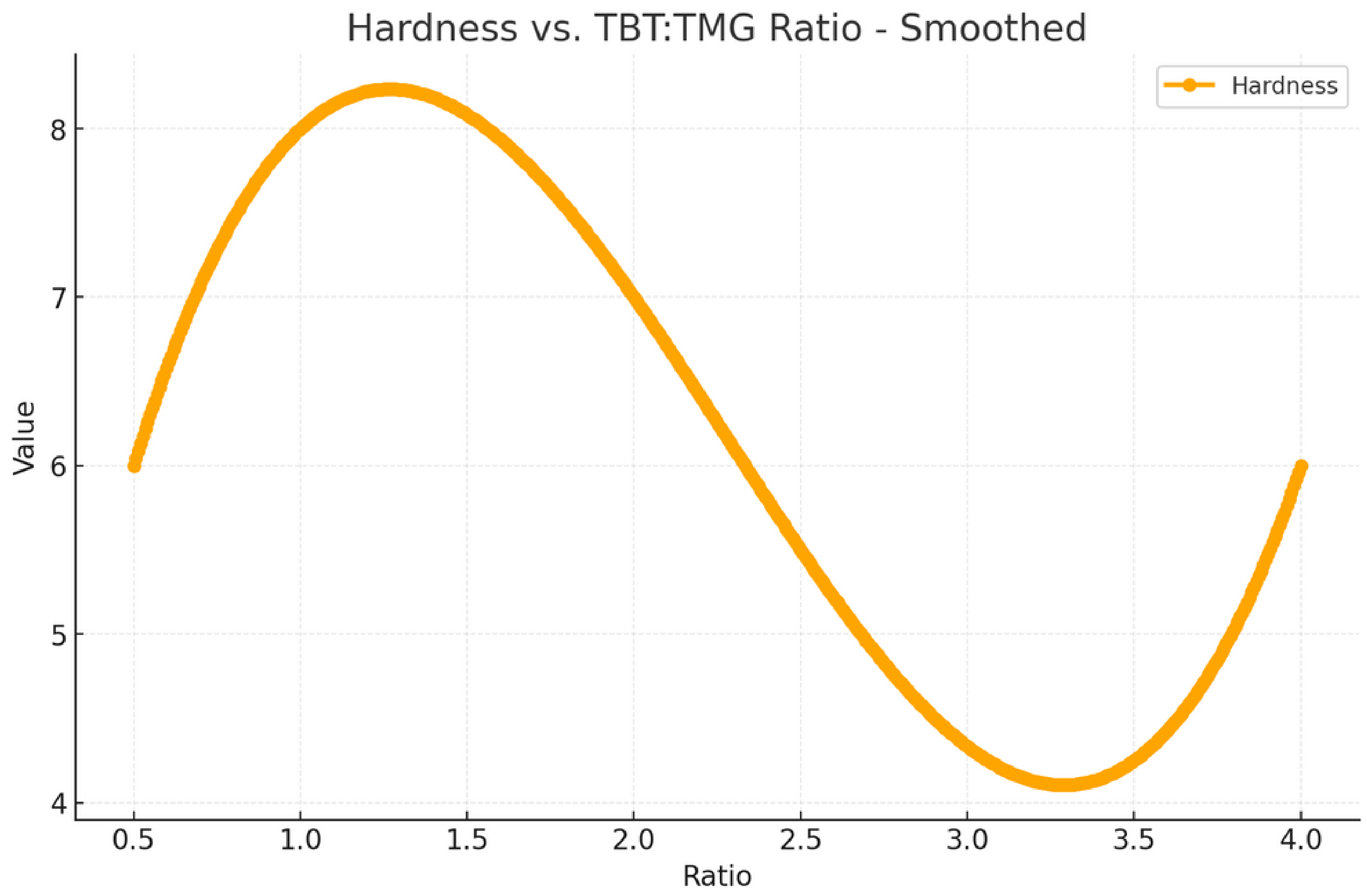
Effect of the catalyst mixing ratio on flexibility and hardness properties





Flexibility is decreasing with an increase in TMG content of the catalyst mixture. Hardness properties vary with the change in the TMG ratio. TBT: TMG ratio optimised at 1: 0.75 ratio.

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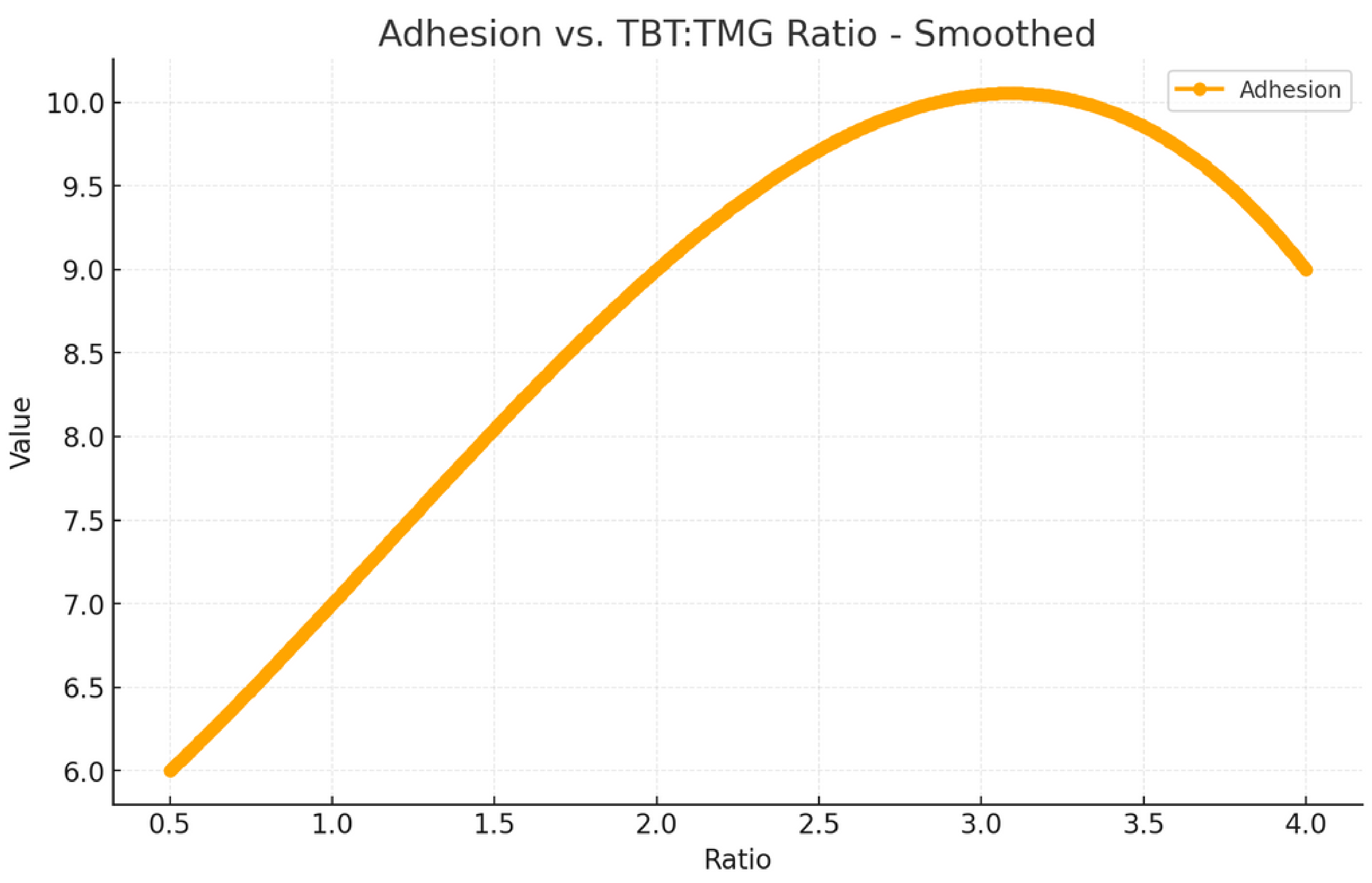
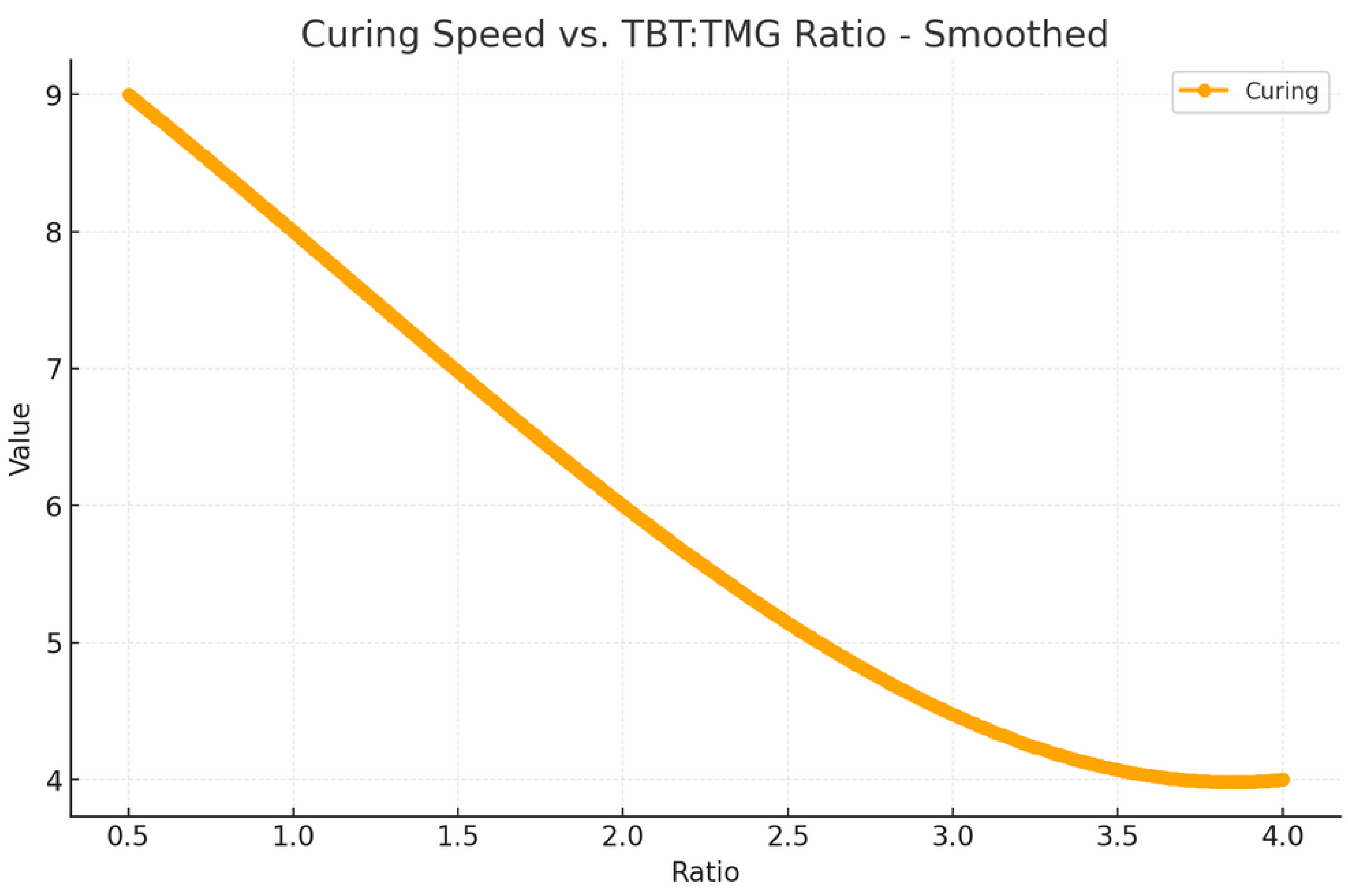
Effect of the catalyst mixing ratio on curing speed and adhesion properties





Adhesion increases with an increase in TBT content up to 3 times that of TMG in the catalyst mixture. Curing speed properties accelerate with the increase in the TMG ratio. TBT: TMG ratio optimised at 1: 0.75 ratio.

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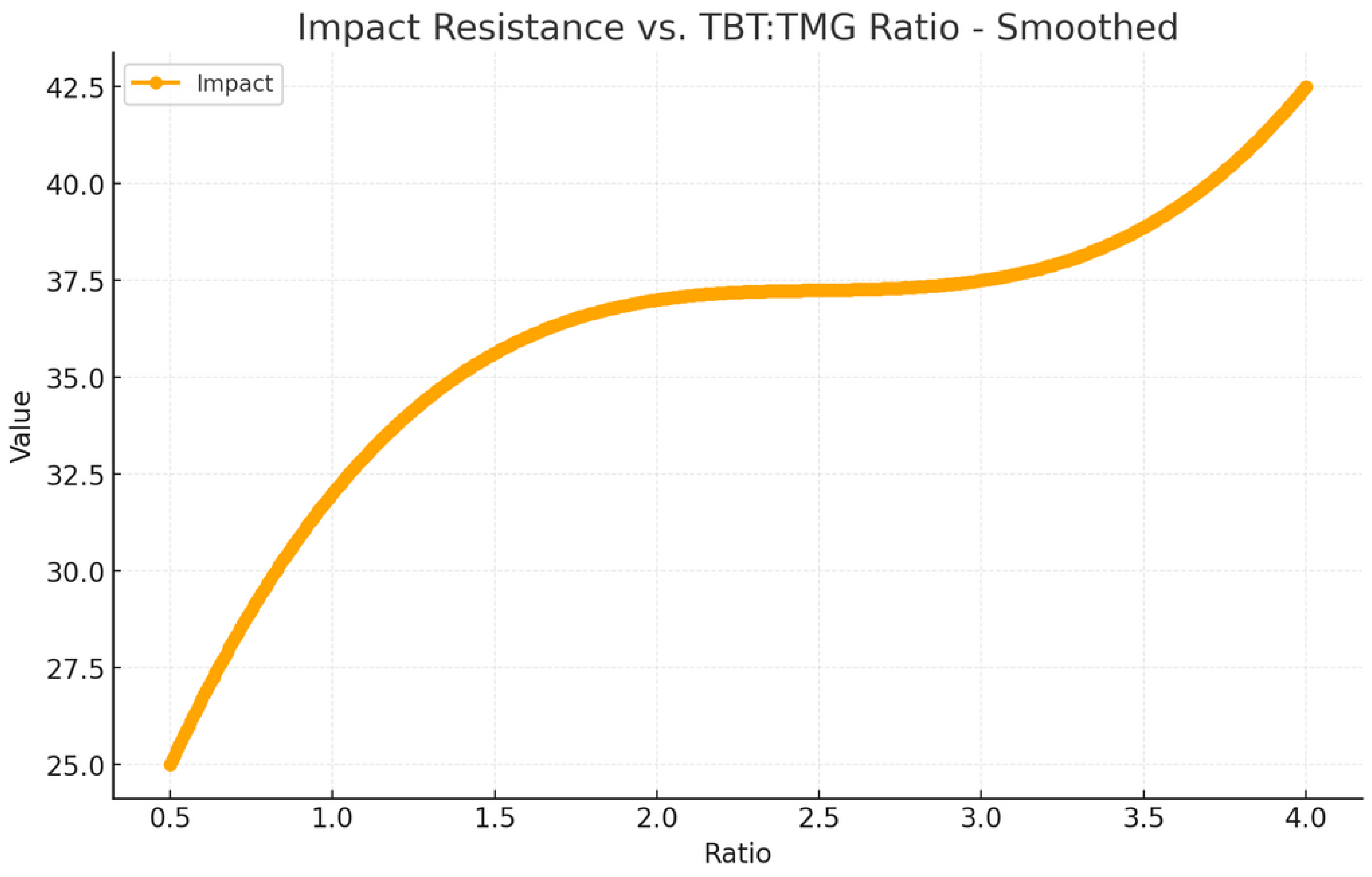
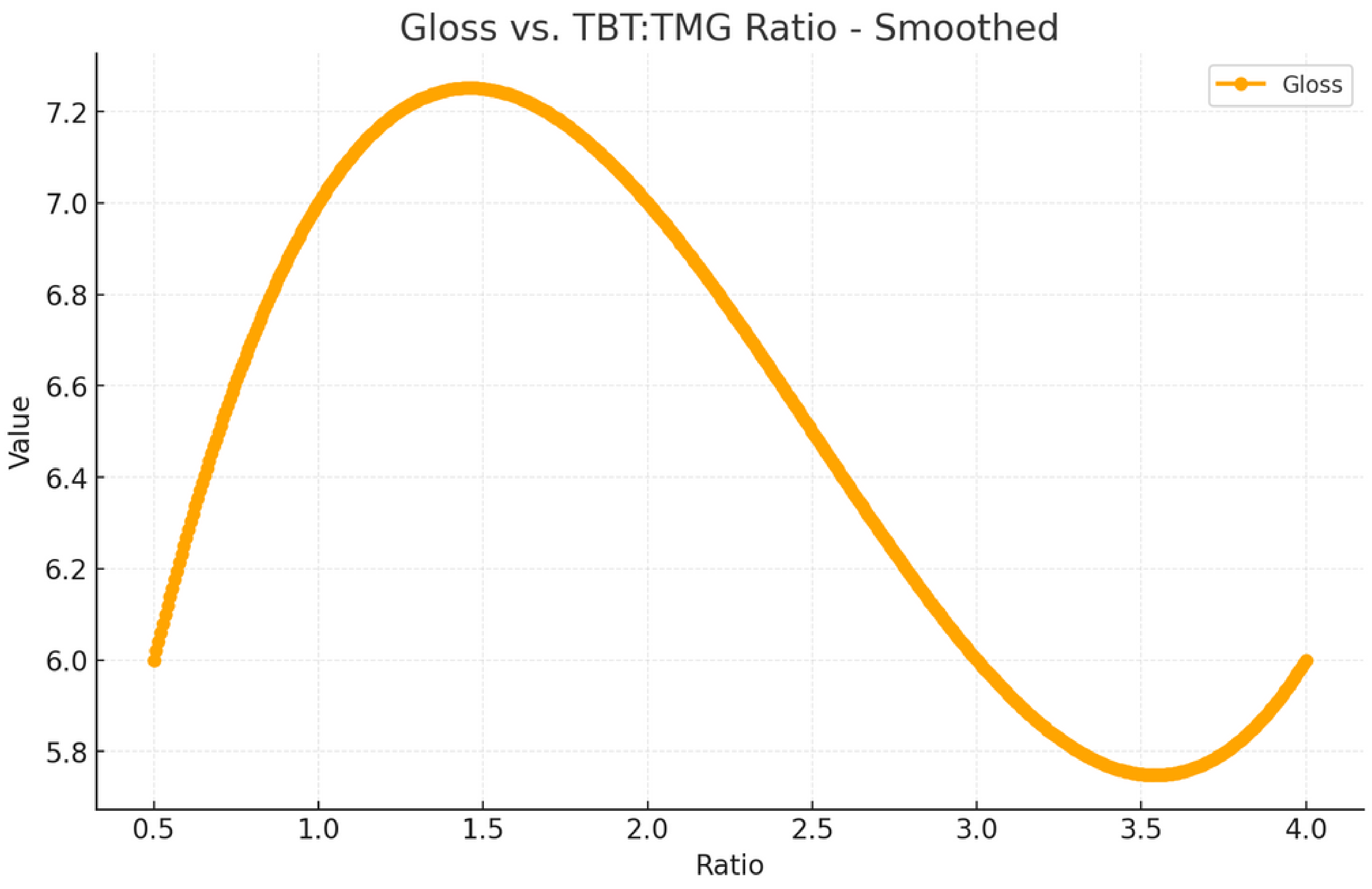
Effect of the catalyst mixing ratio on impact resistance and gloss properties





Impact resistance is increasing with an increase in TBT content of the catalyst mixture. The gloss properties decrease with the increase in the TBT ratio. TBT: TMG ratio optimised at 1: 0.5 ratio

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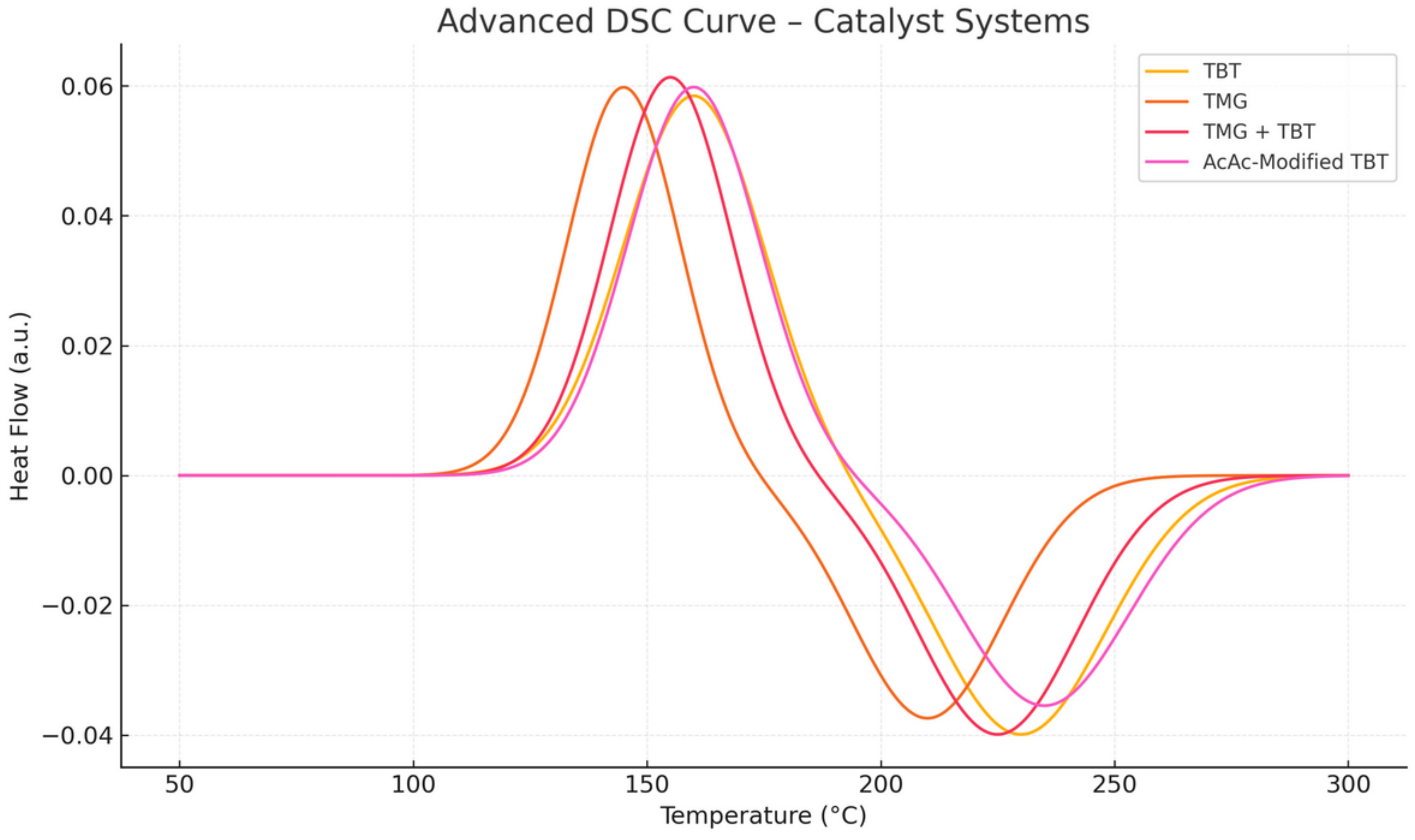
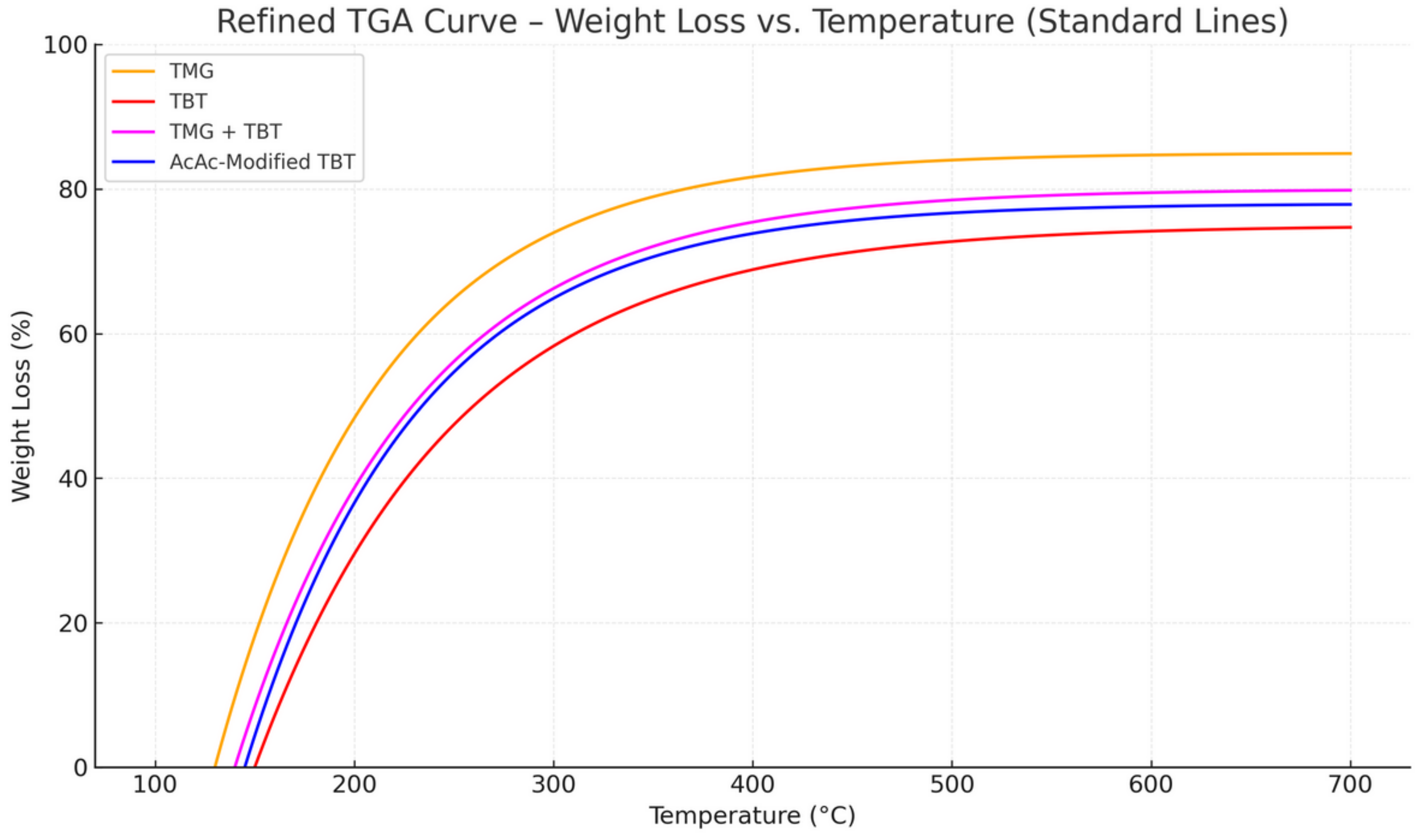
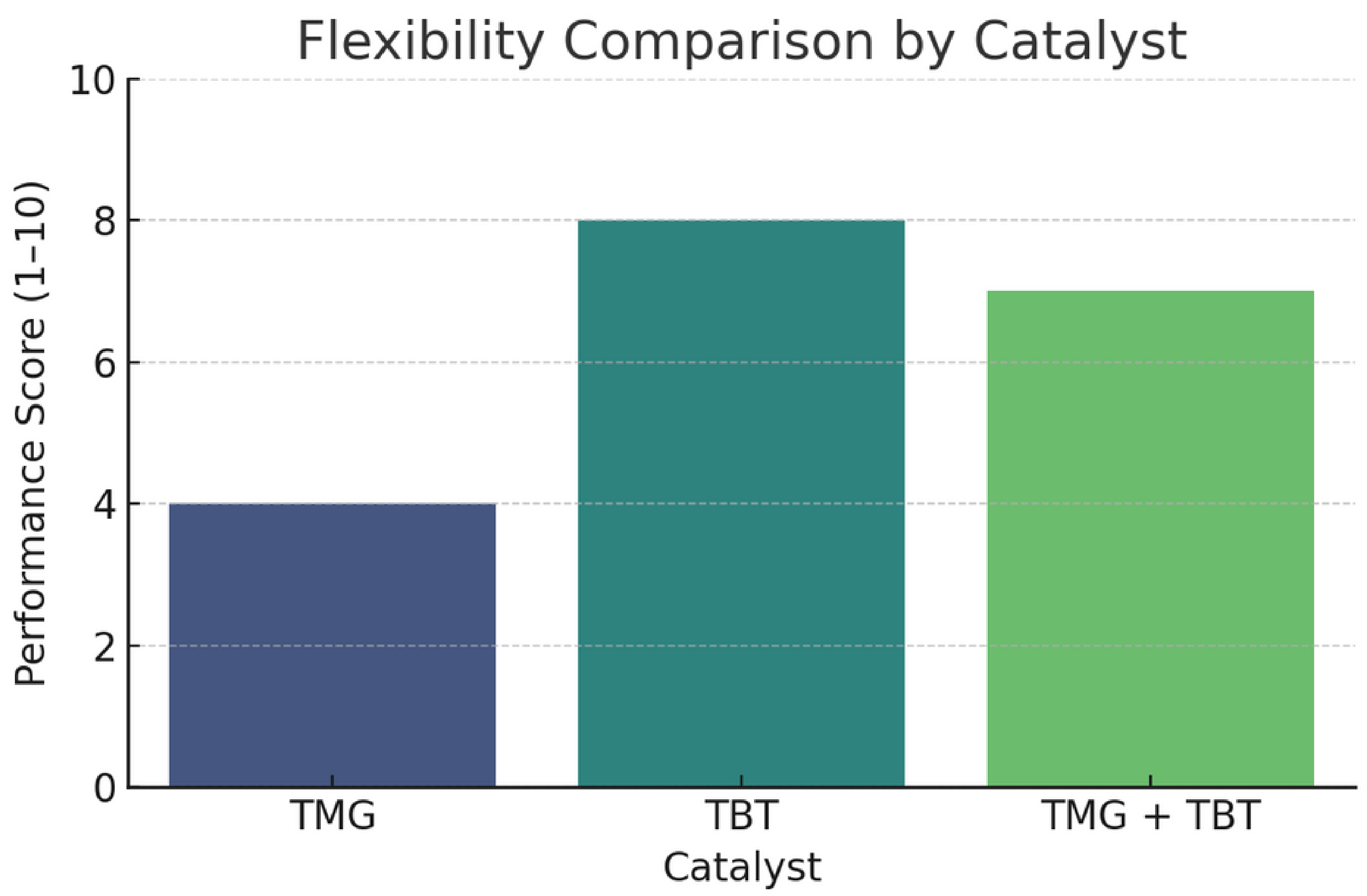
Thermal Analysis Results - TGA & DSC for the catalyst mixing ratio

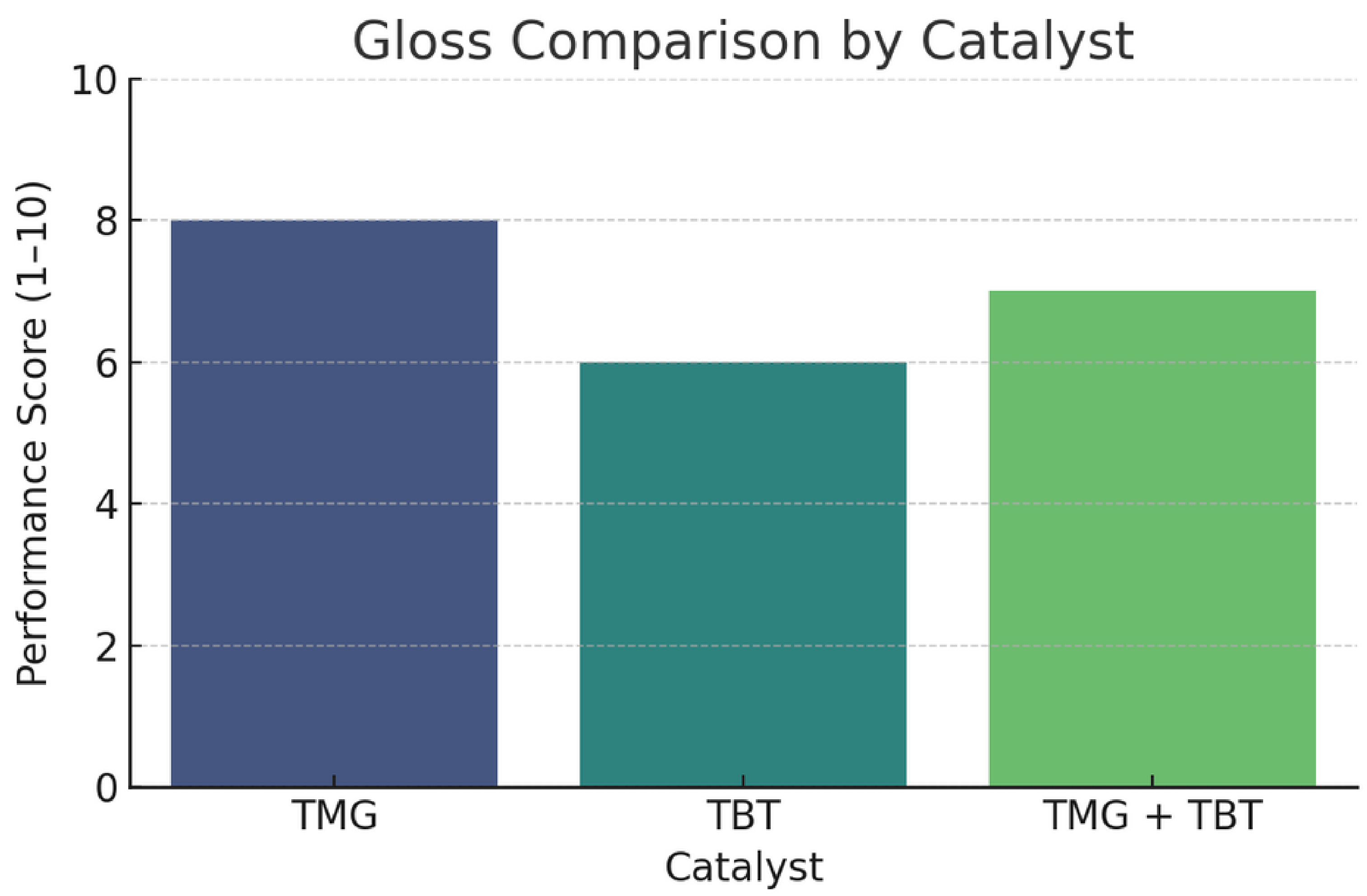




The Tg temperature differs specifically from the catalyst type. The change in the catalyst type changes the Tg of the dry film. Same thing same in the weight loss with temperature increment.

Effect of the catalyst type on flexibility and gloss properties - Methyl:Phenyl Modified Silicone Resin





Methyl-phenyl modified silicone resins should be cured with the catalyst mixture because of their highly non-polar structure. To have good results with only TBT requires the high amount of catalyst dosages.

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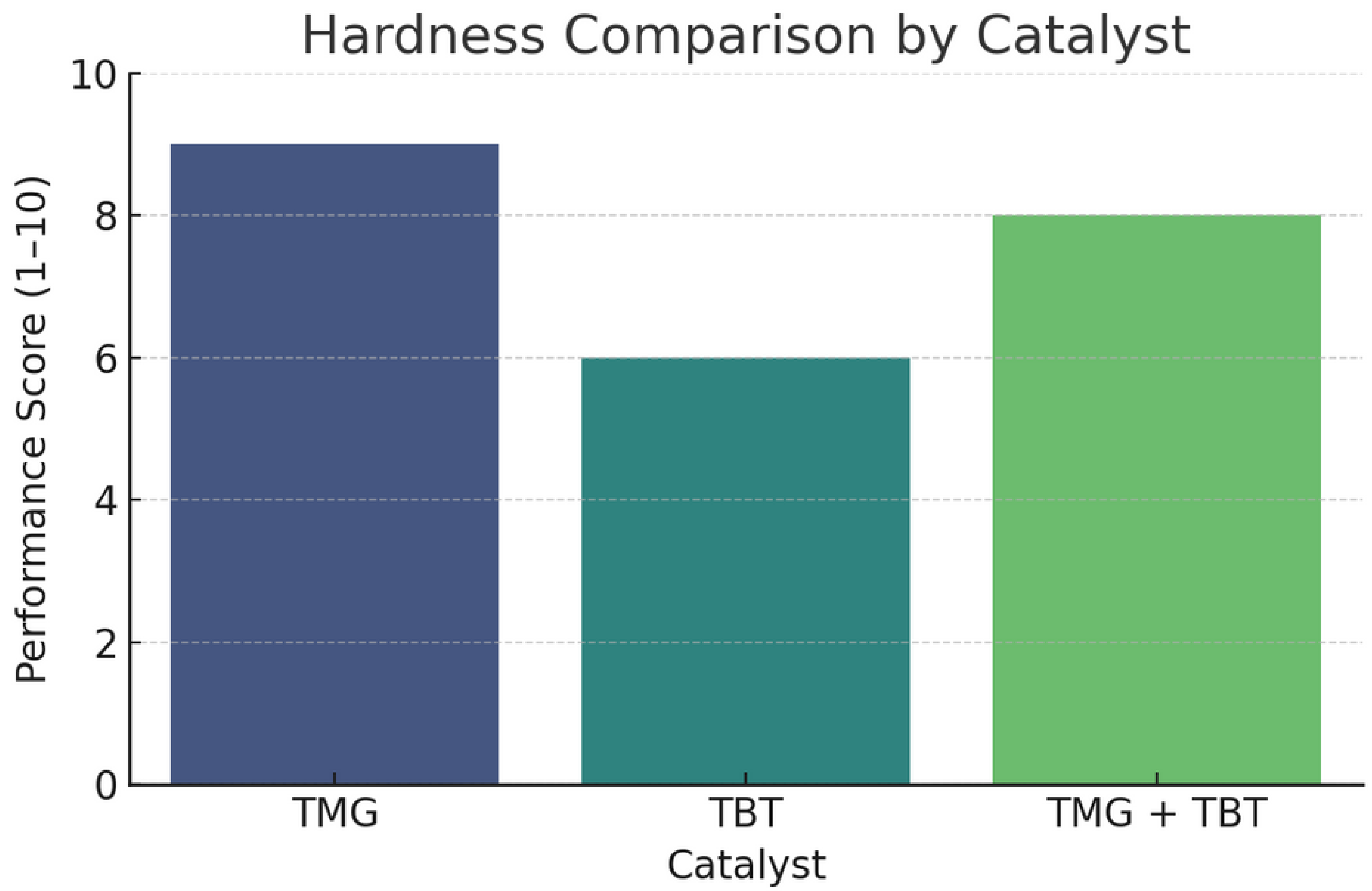
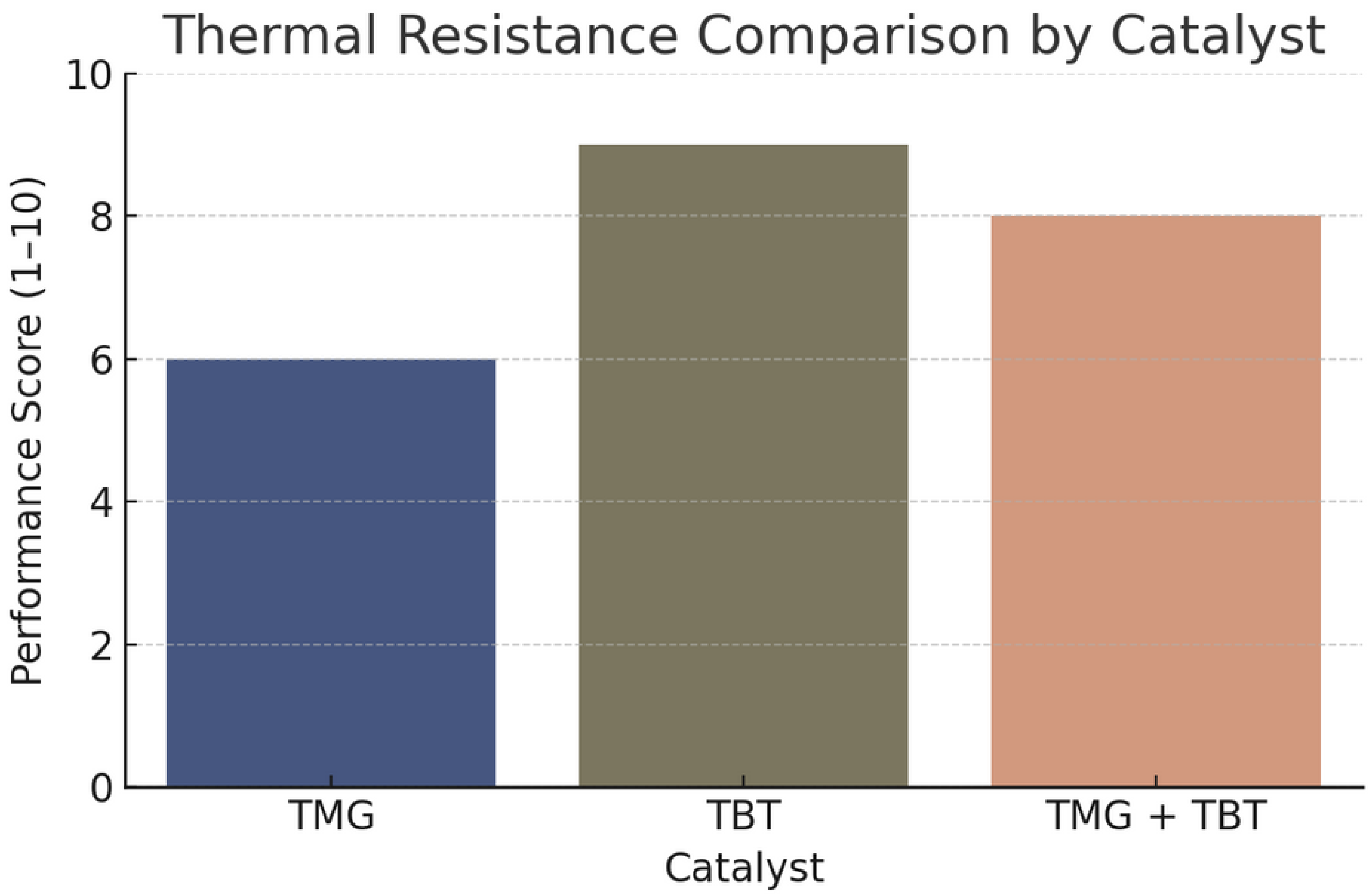
Effect of the catalyst type on hardness and thermal properties - Methyl:Phenyl Modified Silicone Resin



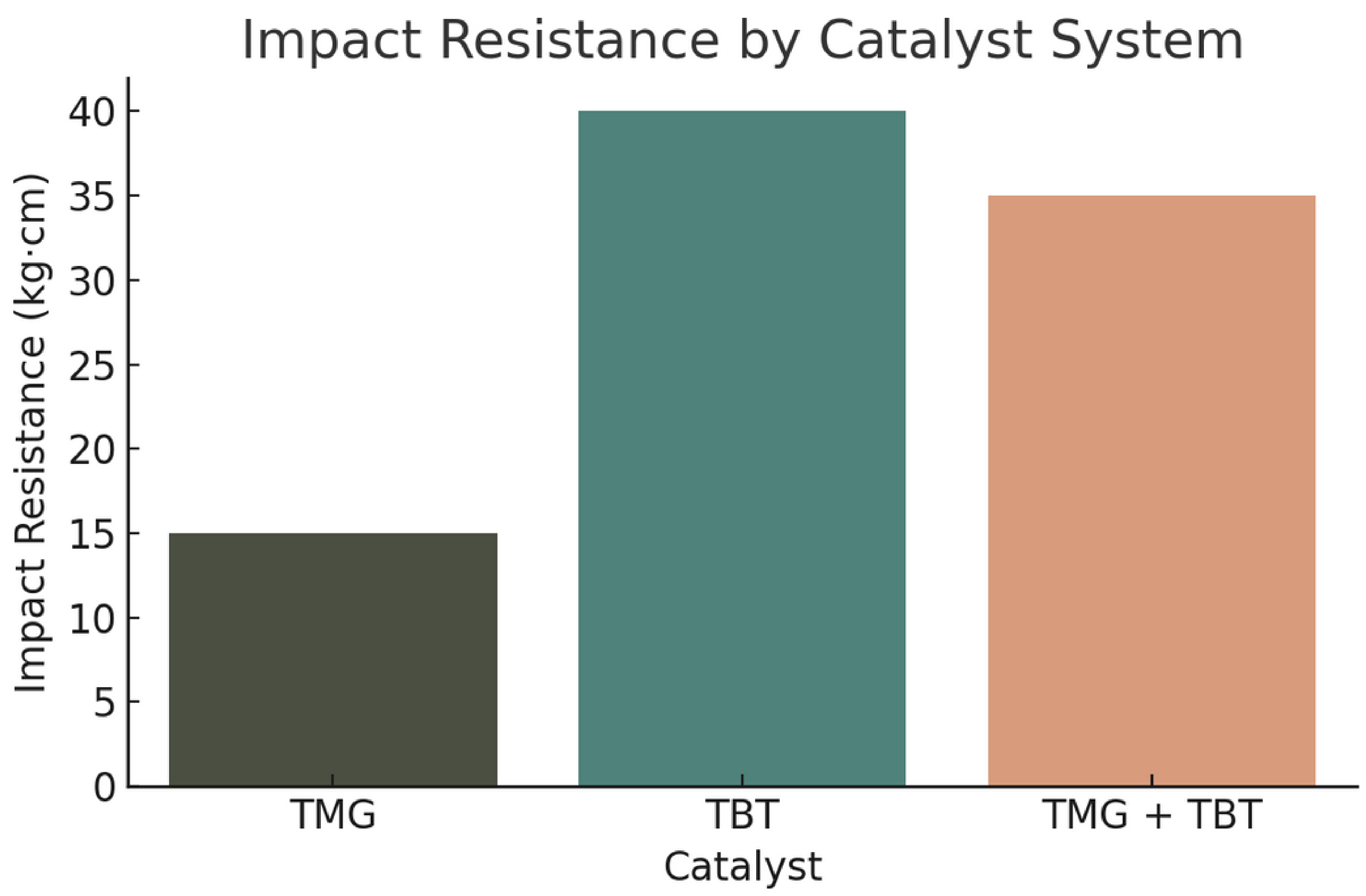


Hardness also increased with TMG, but TMG usage decreases thermal stability. The best option to have both thermal resistance and good hardness with low catalyst usage requires mixing of catalysts.

The impact resistance is improved with TBT usage, at the same time, to have good hardness and fast drying, the system requires to of the TMG.

The best possible option is the mixing of those two different catalysts with optimum ratios.

According to the study, 1:0.75 TBT to TMG ratio gives the best film properties without any defects.



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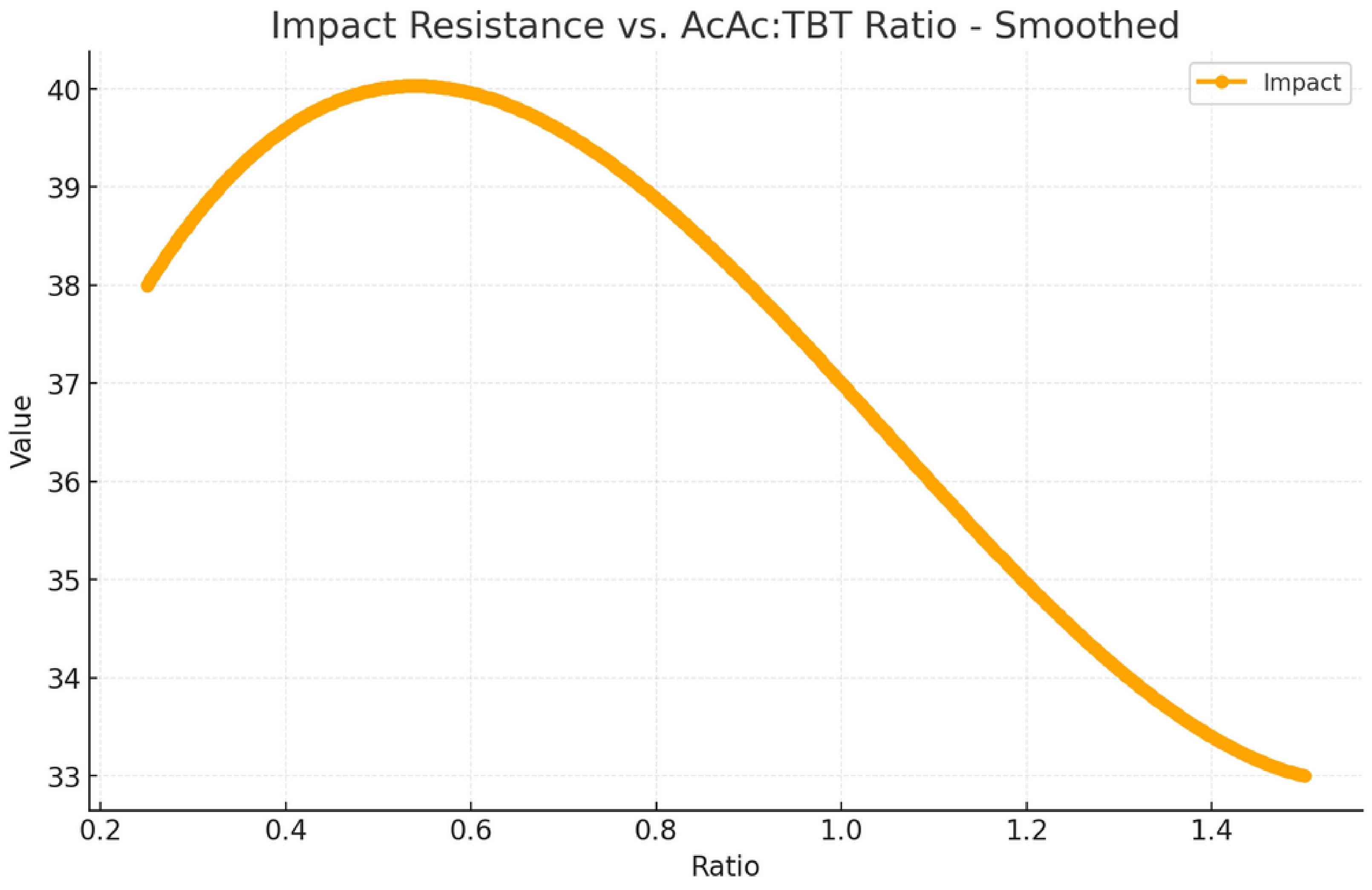
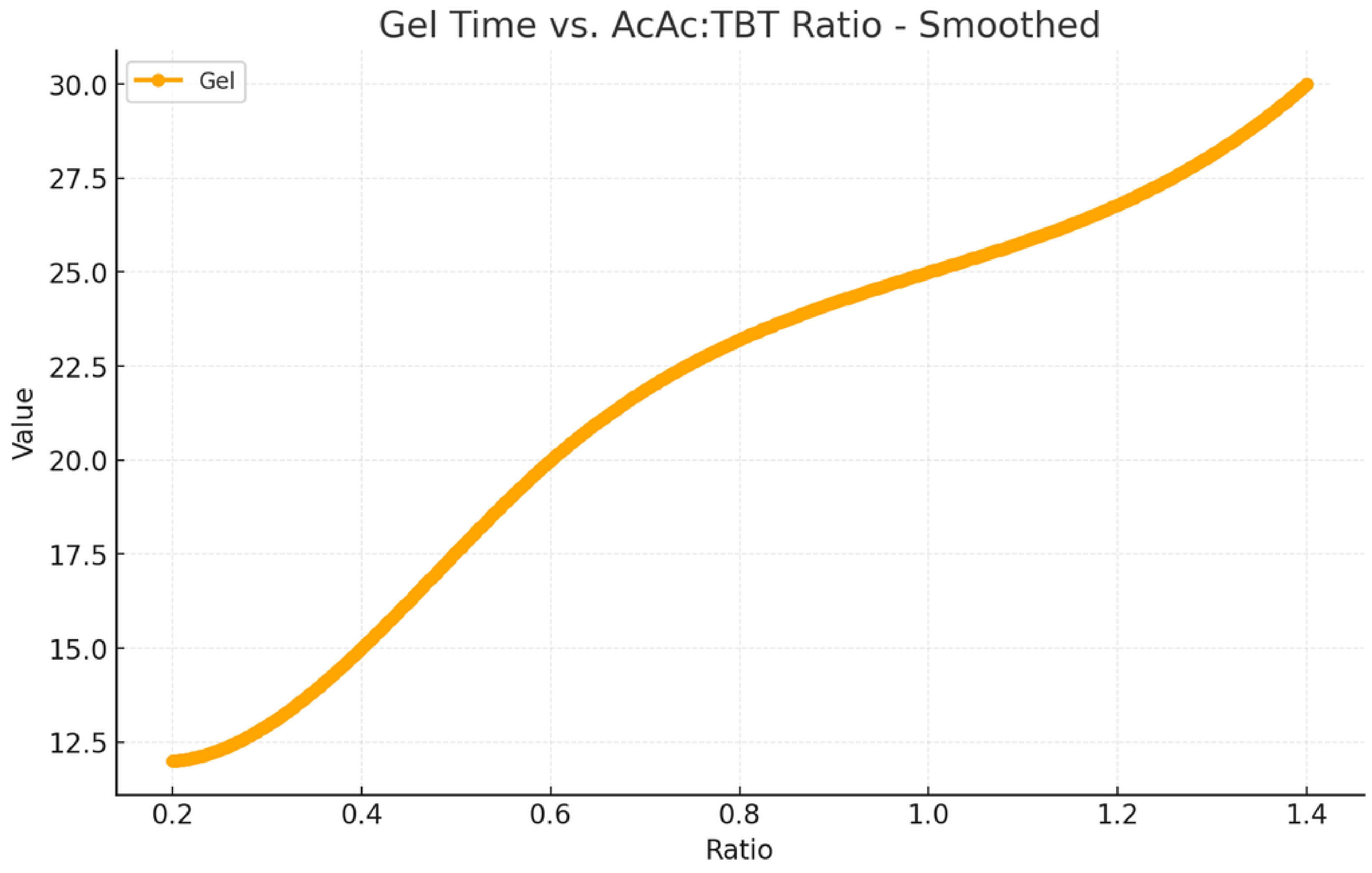
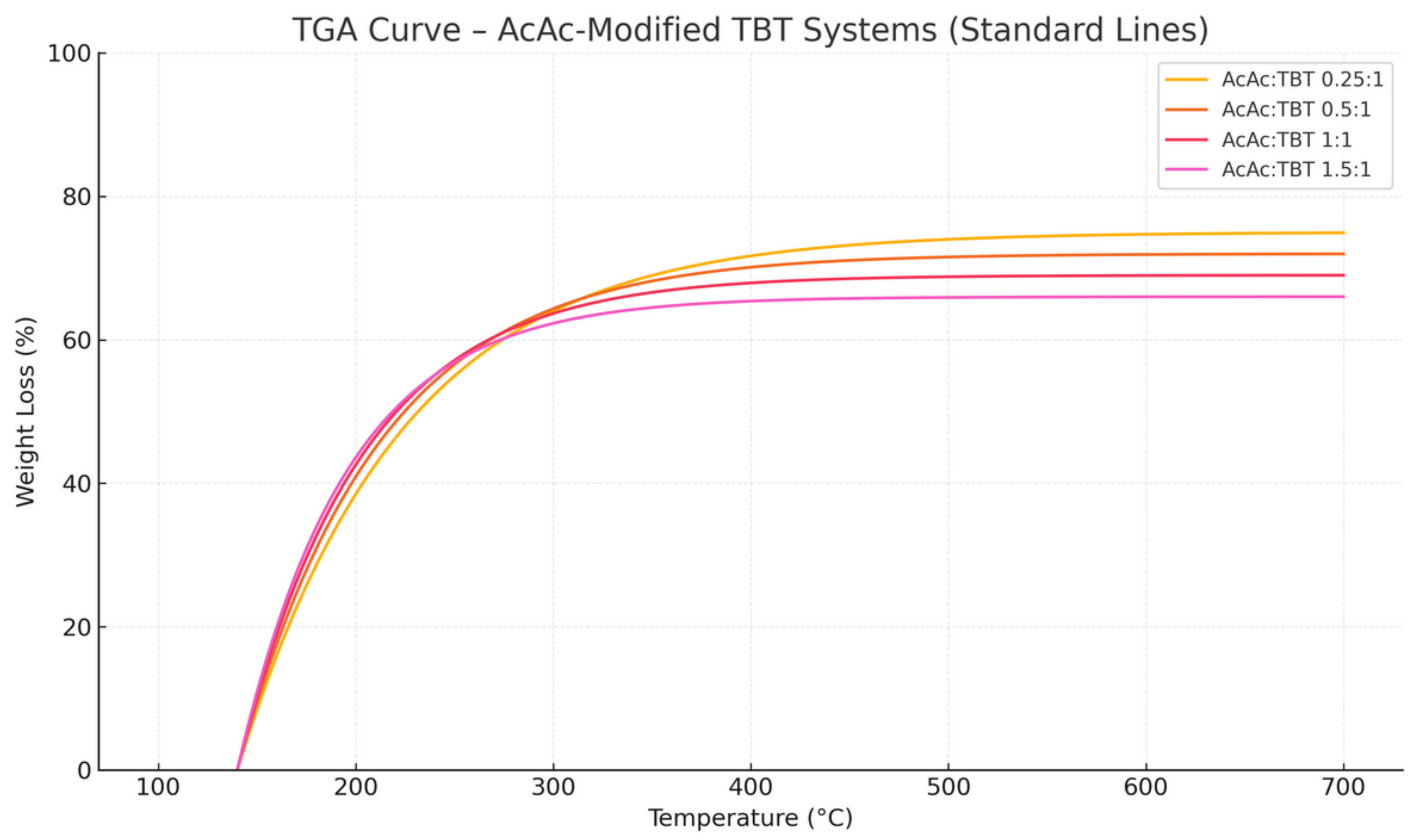
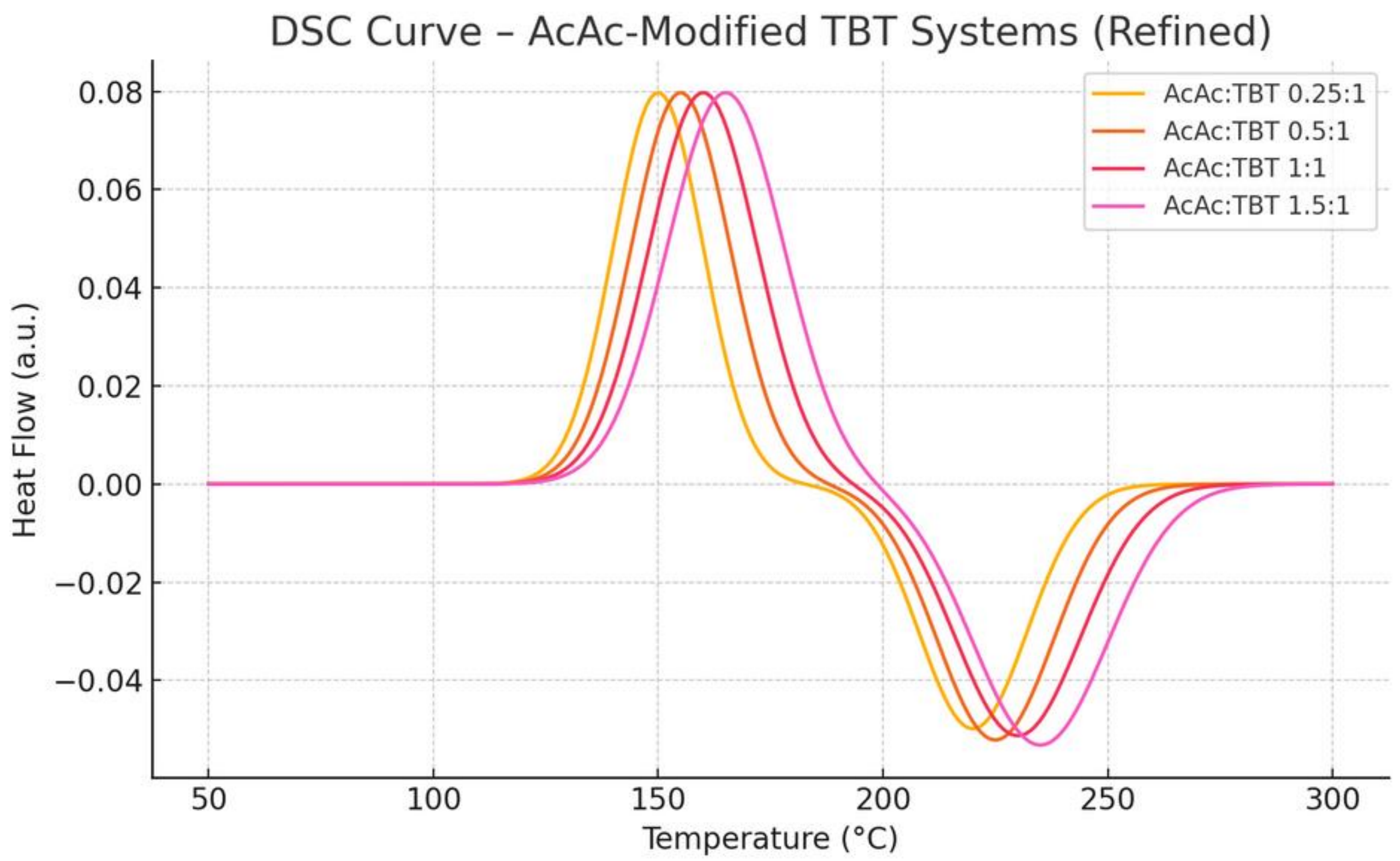
Effect of the treatment of the catalyst on impact resistance and gel time properties - Methyl Modified Silicone Resin



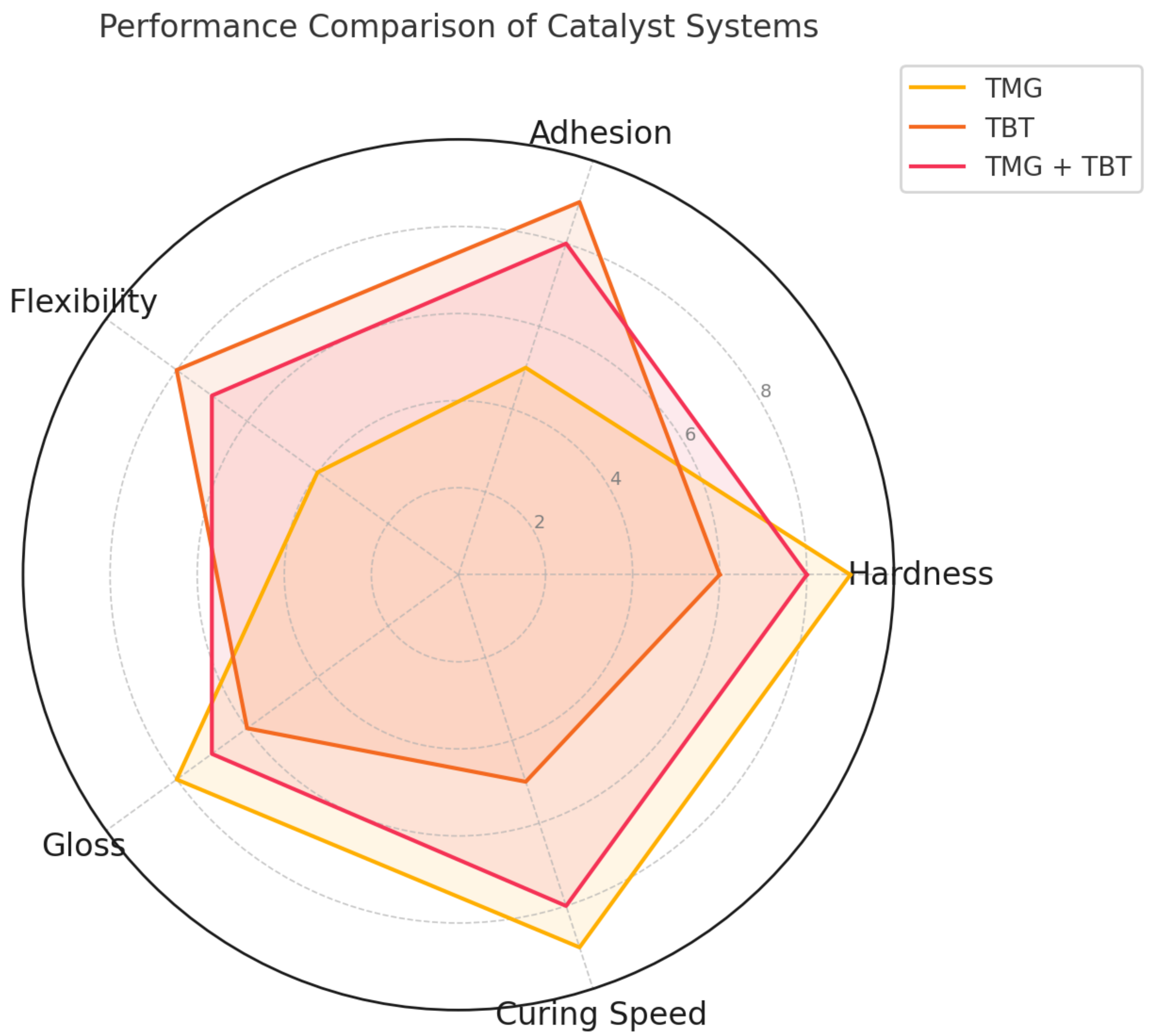


Impact resistance is increasing with an increase in TBT treatment content of the catalyst. The gelation time increased with the increase in the TBT treatment ratio. TBT: AcAc ratio optimised at 1: 0.8 ratio





The Tg temperature differs specifically from the catalyst ratio. The change in the catalyst ratio changes the Tg of the dry film. Same thing same in the weight loss with temperature increment.


Performance Comparison of Catalyst Systems
TMG
TBT
TMG + TBT
Adhesion
Flexibility
Hardness
Gloss
Curing Speed
2
4
6
8

1. Catalyst Impact on Film Performance

TMG provides fast curing and surface hardness, but limited flexibility
TBT delivers better adhesion and flexibility, but cures slower

2. Acetylacetone-Modified TBT

Improved catalyst stability
Extended gel time with minimal performance trade-offs
Better control in ambient curing environments

3. Dual Catalyst System

Synergistic behavior between TMG and TBT
Achieved a balance of mechanical and curing properties
Dual systems provide a tailorable approach for different performance targets

4. Broader Implications

Offers formulation flexibility for diverse applications (e.g., industrial coatings, electronics, heat-resistant surfaces)
Customizable cure profiles = better process control for manufacturers

5. Future Work

Explore other chelating agents beyond AcAc
Long-term durability and aging studies
Scale-up validation and pilot production trials