Strategies for Improving the 'Back-end' Reactivity of Bismuth Carboxylate Catalysts

Bismuth carboxylates are known to offer excellent 'front-end' reactivity as gelling catalysts in urethane applications. However, they are also associated with a lack of 'back-end' reactivity, which affects important manufacturing properties for polyurethane elastomers such as demolding time, residual tackiness, and hardness buildup. To address these challenges, REAXIS® has investigated how excess complimentary carboxylic acid and heterobimetallic complexes influence 'back-end' curing in a model polyurethane elastomer formulation.

A bismuth carboxylate's catalytic behaviors can be tuned by varying the amount of free acid in the catalyst solution.[1]

TABLE 1. Model polyurethane elastomer formulation

Component	pphp
Polypropylene oxide triol[a]	66.3
Trifunctional polyether polyol[b]	14.1
Ethylene glycol[c]	2.5
Catalyst	0.2
Polymeric methylene diphenyl diisocyanate[d]	17.0[e]

Cure Schedule: 30 min @ 50 °C; 3.5 h @ 25 °C
[a] OH number = 26.0 – 28.0
[b] OH number = 28.0
[c] OH number = 160 - 165
[d] NCO content = 31.5%
[e] NCO/OH = 1.05

This principle was investigated using the model polyurethane elastomer formulation in Table 1. The bismuth-derived catalysts in this study include REAXIS® C716, REAXIS® C3208, and REAXIS® C3209, where REAXIS® C3209 is a low-viscosity version of REAXIS® C3208. Their catalytic performance was compared to that of the industry standard, dibutyltin dilaurate (DBTL, REAXIS® C218). The amount of excess neodecanoic acid within the formulation at 0.2 wt% catalyst loading was determined to be ~0.08% (REAXIS® C716), ~0.06% (REAXIS® C3208), and ~0.02% (REAXIS® C3209). While the presence of excess neodecanoic acid may affect properties negatively,[2,3] it was found that larger quantities of excess neodecanoic acid led to accelerated rates of Shore A hardness build-up, which in the case of REAXIS® C716 mimic that of DBTL (Figure 1A).

While increasing metal content typically has a strong correlation with increased reactivity, bismuth is unique in this case due to additional carboxylic acid mechanistically assisting polyurethane formation through protonation and consumption of a metal-carbamate intermediate, instead of acting as a simple diluent.[4] The difference in behavior of REAXIS® C716, REAXIS® C3208, and REAXIS® C3209 demonstrates this principle, as the bismuth content (%) for these catalysts

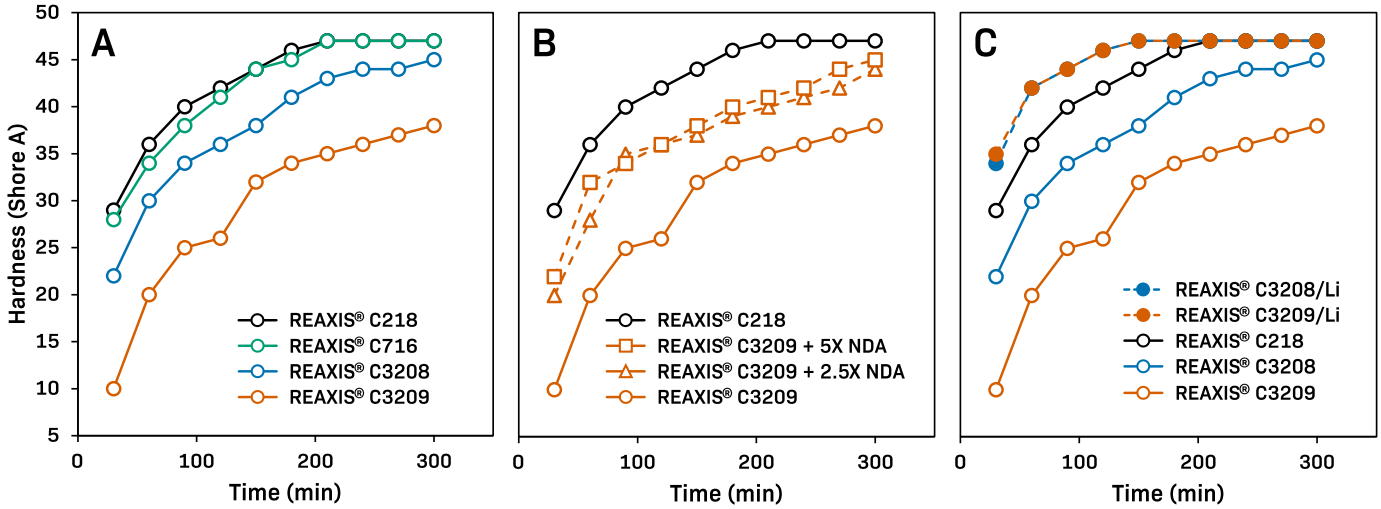

FIGURE 1. Shore A Hardness over time for a model polyurethane elastomer catalyzed by (A) bismuth carboxylates with varying amounts of neodecanoic acid, (B) low-acid containing bismuth carboxylates doped with excess complimentary carboxylic acid, and (C) bismuth-lithium heterobimetallic complexes with industry standard DBTL as a reference.

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are 17.1, 20.2, and 19.0%, respectively. This small yet powerful difference and its correlation to reactivity is a perfect example of how dramatically a catalyst may affect a formulation. This assist does not result in a faster gelling for this given formulation but does result in a more efficient generation of hardness.

While the presence of free carboxylic acid mechanistically affects the polyurethane mechanism, the acid : bismuth ratio during the synthesis of the catalyst itself is important in determining the overall structure and, therefore, reactivity of the catalyst. Bismuth carboxylates can adopt structures comprising a range of complex, multi-metallic centers – from structures containing more bridging carboxylate units to more discrete, mono-metallic species.[5,6]

To investigate this concept, the lowest excess acid containing REAXIS® C3209 was doped with additional neodecanoic acid to mimic the acid levels of REAXIS® C3208 and REAXIS® C716. The catalyst loading for the neodecanoic acid doped versions of REAXIS® C3209 was adjusted to match the metal content of REAXIS® C3208 and REAXIS® C716 (Figure 1B). The same Shore A Hardness study was performed and revealed a considerable change in hardness buildup, which was similar to that of REAXIS® C3208. However, this additional free acid was not enough to match the behaviors of pure REAXIS® C716, which most likely contains unique structures that were formed based on its synthetic preparation. This demonstrates that the addition of complimentary carboxylic acid can improve hardness but the microstructure of the catalyst should also be considered.

The behaviors of bismuth-lithium heterobimetallic[7] complexes were also investigated. These unique complexes were found to have improved reactivity when compared to standard bismuth catalysts. It was observed that the Shore A hardness buildup for a moderately soft polyurethane formulation could be accelerated to exceed the hardness profile of DBTL for each heterobimetallic bismuth-lithium complex (Figure 1C). Initial gel time screening using a separate 2-component polyurethane elastomer formulation consisting of a 2° polypropylene oxide-based triol and polymeric methylene diphenyl diisocyanate (pMDI) (NCO/OH = 1.05) were measured. Despite possessing lower metal content, a synthesized heterobimetallic Bi/Li complex (11% Bi, 0.9% Li) was more reactive than both the individual lithium-based catalyst (2% Li) and the bismuth carboxylate catalysts (20% Bi) (Figure 2).

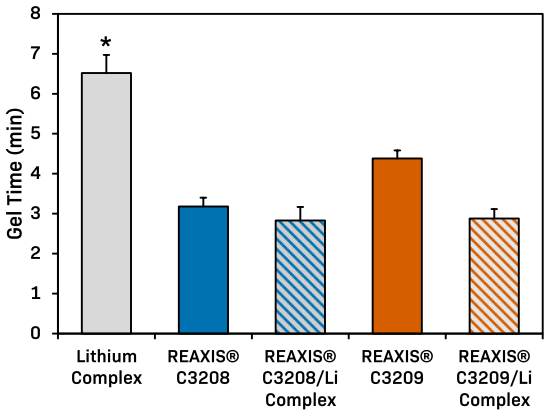

FIGURE 2. Gel times for lithium, bismuth, and lithium-bismuth heterometallic complex catalysts at 0.06 wt% loading in a 2-component polyurethane elastomer. *Catalyst loading increased to 0.1 wt% to obtain gel times < 10 min with minimal deviation.

The REAXIS® bismuth product portfolio includes several bismuth neodecanoate (C716, C3208, C3209) and bismuth octoate based catalysts (C3210 and C3202LA). Bismuth/Zinc blends, which were beyond the scope of this bulletin, are also offered by REAXIS® (C708 and C717). Additional water-tolerant bismuth non-carboxylates are available (C739W50, C739E50, C3211EXP, C3212EXP). Customized product design and sampling is available upon request.

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