CABOT

FUMED METAL OXIDES

CAB-O-SIL® Treated Fumed Silicas for Polyols Used in Polyurethanes

CAB-O-SIL® TREATED FUMED SILICAS FOR POLYOLS USED IN POLYURETHANES

Contents

Liquid 2-component (2K) polyurethanes (PURs) comprise an extremely useful class of thermoset resins utilized by both adhesive and coating formulators. The two components of the system are distinctly different and are only mixed prior to use. One component contains the isocyanate; the second component contains the polyol.

The polyol is always an alcohol with multiple hydroxyl groups. These groups are available for the desired organic reaction with the isocyanate after the two components are mixed together. Common polyols for 2K PUR systems include polyethers, polyesters, and hydroxyl-terminated polybutadienes

Recognizing the formulator's challenge

The formulator selects a thixotrope additive (such as fumed silica) for two important reasons:

- To provide acceptable sag resistance for the application of the PUR prior to curing.
- To facilitate the effective mixing of the two components by thickening the polyol. Homogeneity is reached most effectively when the mixed components share similar viscosity profiles.

Unfortunately, the two reasons are not necessarily mutually supportive. Often, the formulator must balance trade-offs between properties such as:

- Degree of thickening
- Ease of dispersion
- Clarity of dispersion

This applications guide will assist the formulator to select the appropriate fumed silica additive for the desired formulation chemistry and mix of performance features.

Case studies

Polyether

Polyethers are the most common class of polyols used in polyurethanes. In general, polyether polyols are affordable and resistant to alkalis, have a low viscosity, and impart good low temperature flexibility.[1]

The relative viscosity as a function of shear rate for various CAB-O-SIL® fumed silicas compounded into a polyether polyol is presented in Figure 1a, and the trade-offs among properties for the various treated fumed silica products are illustrated in Figure 1b. TS-720 fumed silica offers excellent thickening in this system; TS-530, TS-610 and M-5 fumed silicas result in little thickening, as illustrated in Figure 1a. Selection of a fumed silica for a PUR involves trade-offs that require a formulator to prioritize properties for its specific application. For example, if thickening and ease of dispersion are most important, Figure 1b indicates that TS-530 fumed silica may be a good candidate to consider given its thickening ability and that it takes less time to process relative to TS-720 fumed silica. If clarity is most important, TS-610 fumed silica yielded very transparent compounds.

Figure 1a: Relative viscosity as a function of shear rate for various fumed silica products at 6 wt.% in a polyether polyol[2]

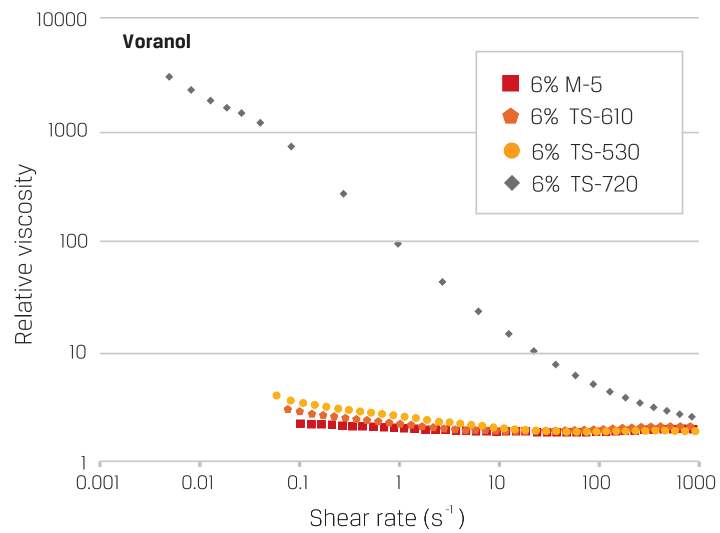
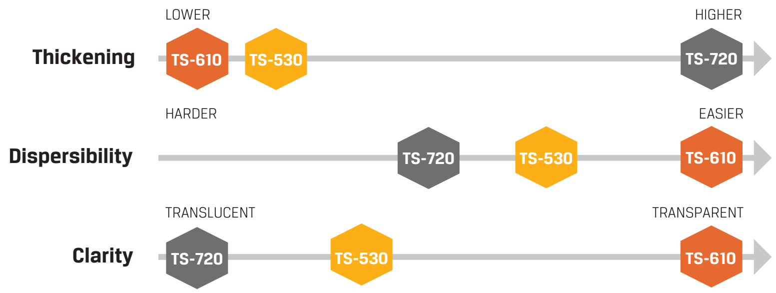


Figure 1b: Property trade-offs between fumed silica products in a polyether polyol



Polyester

Polyesters are a common class of polyols used in polyurethane applications. Polyester polyols are advantageous because they offer good solvent resistance, good adhesion and excellent mechanical properties.[1,3]

The relative viscosity as a function of shear rate for various CAB-O-SIL® products compounded into the polyester polyol is presented in Figure 2a. In this case, TS-720 fumed silica offers the greatest efficiency in thickening this system followed closely by TS-530 fumed silica. Similar to the polyether, TS-610 and M-5 fumed silicas resulted in little thickening in this polyester. Regarding property trade-offs and product selection, as indicated in Figure 2b, TS-530 fumed silica offers a balance of good thickening and moderate dispersion time.

Figure 2a: Relative viscosity as a function of shear rate for various fumed silica products at 6 wt.% in a polyester polyol[2]

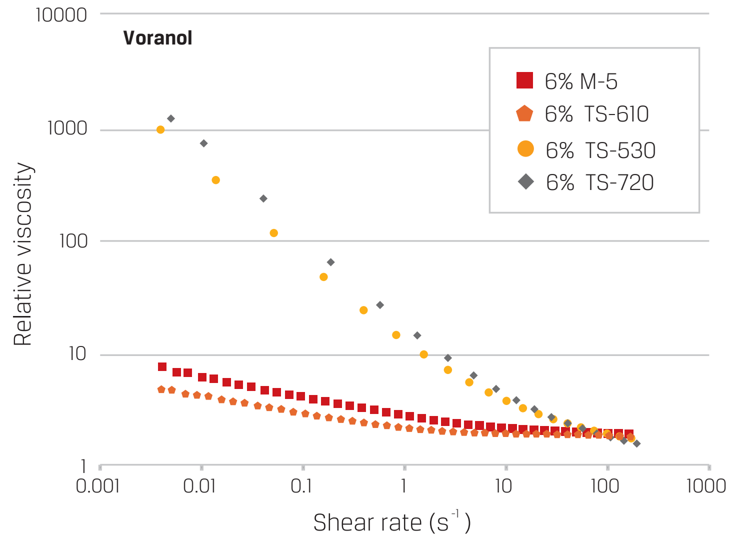
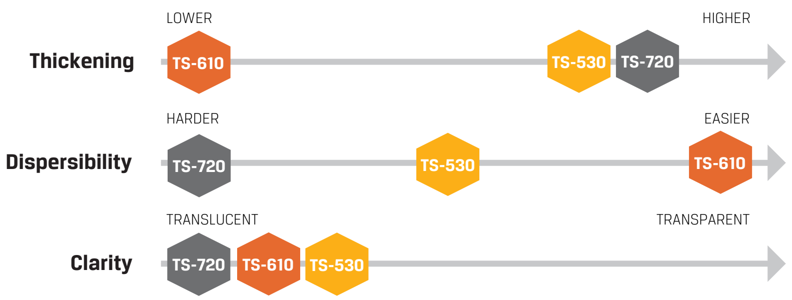


Figure 2b: Property trade-offs between Cabot fumed silica products in a polyester polyol



Storage stability

Storage stability in the compounded product is highly desired in many applications. An aging study was performed on TS-720 fumed silica and in a polyether and polyester polyol to assess storage stability. Compounded samples were initially evaluated on the day of manufacture. The samples were subsequently aged in a 60ºC oven for 4 weeks; the rheological performance of the samples was re-evaluated. It should be noted that all rheological measurements were performed at 25ºC.

The initial and aged relative viscosity as a function of shear rate for TS-720 fumed silica in a polyether and polyester polyol are presented in Figures 3a and 3b, respectively. Overall, TS-720 fumed silica performed well in each polyol and retained a significant amount, ca. 85%, of its initial thickening ability in the polyether polyol after 4 weeks of 60ºC aging, as indicated in Figure 3a. Similarly in Figure 3b, TS-720 fumed silica in the polyester polyol retained its thickening ability over the time period tested.

Polybutadiene

Polybutadienes are a common class of polyols used in polyurethane applications. Polybutadiene polyols are advantageous because they offer good flexibility, good adhesion, and low moisture absorption.[4]

The relative viscosity as a function of shear rate for various CAB-O-SIL® products in a polybutadiene polyol is presented in Figure 4a. TS-720 fumed silica is the most effective thickening agent in this system. TS-530, TS-610 and M-5 fumed silicas provided little to no thickening in this polyol. If dispersion time or clarity are important, TS-610 or TS-530 fumed silicas would be appropriate as indicated in Figure 4b.

Figure 4a: Relative viscosity as a function of shear rate for various fumed silica products at 6 wt.% in a polybutadiene polyol[2]

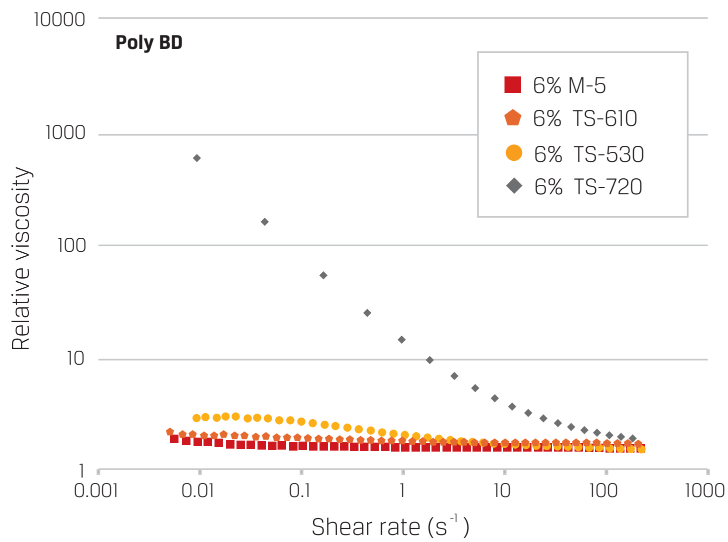


Figure 4b: Property trade-offs between Cabot fumed silica products in a polybutadiene polyol

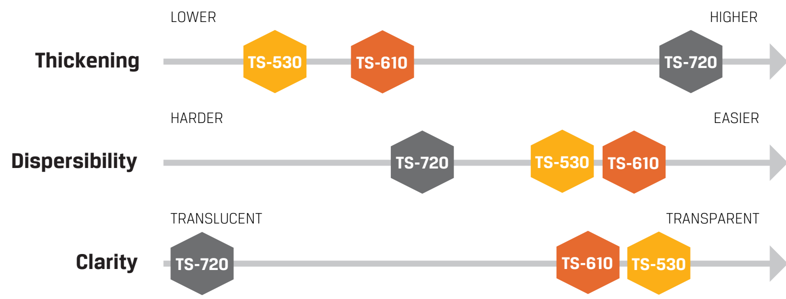
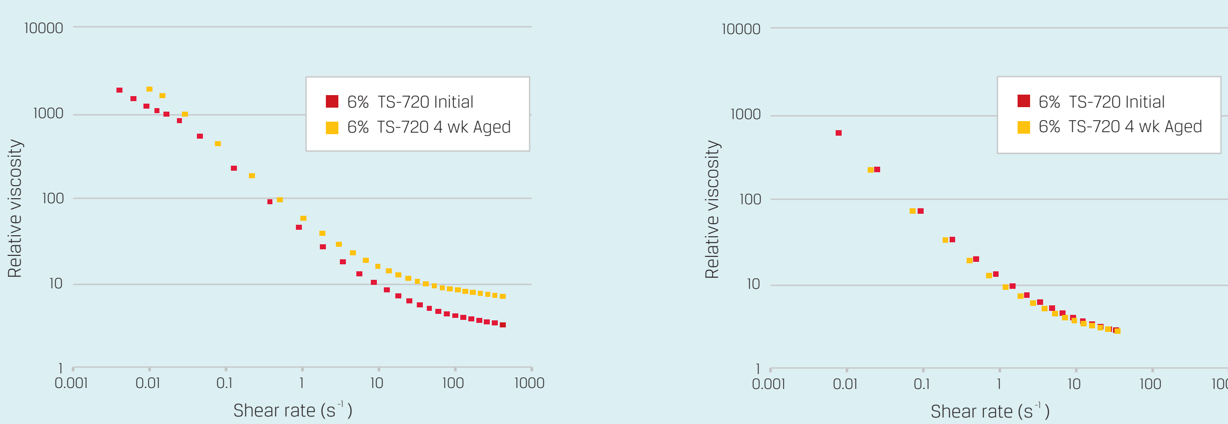


Figure 3: Relative viscosity as a function of shear rate for Cabot fumed silica product at 6 wt.% in:

a) Polyether

b) Polyester polyol



Soy

Soy polyols are part of a larger family of natural oil polyols. Natural oil polyols are an area of growing interest due to efforts to increase the renewablity or sustainability of consumer products. Soy polyols are being used to partially replace polyether polyols in polyurethane formulations and have been observed to enhance the mechanical performance relative to their conventional counterparts.[5]

The relative viscosity data as a function of shear rate for various CAB-O-SIL® products in the soy polyol is presented in Figure 5a. TS-720 fumed silica resulted in the best thickening in this polyol. The remaining products yielded little thickening in this system. The overall results for the soy and polybutadiene polyols are very similar. As a result, the trade-offs discussed in the polybutadiene section are applicable here as well.

Figure 5a: Relative viscosity as a function of shear rate for various Cabot fumed silica products at 6 wt.% in a soy polyol[2]

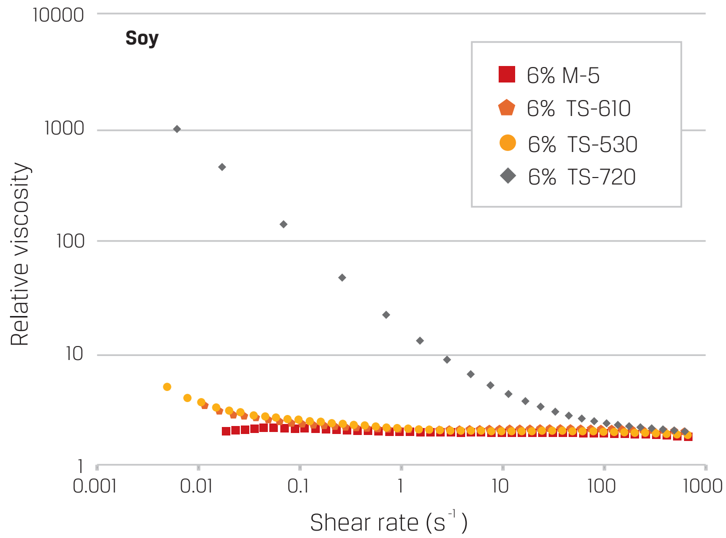
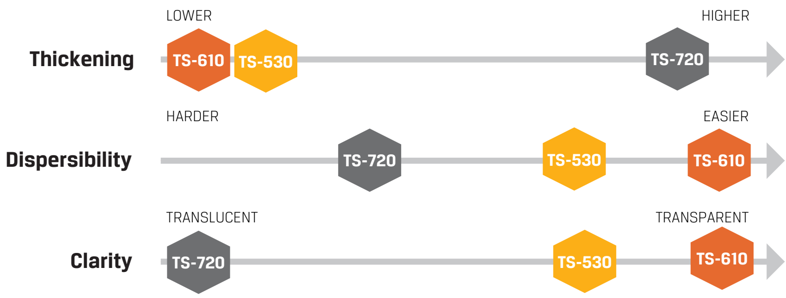


Figure 5b: Property trade-offs between Cabot fumed silica products in a soy polyol



1 General Polyurethane Information, www.wernerblank.com
2 All samples were compounded using a Hauschild DAC 150 Speedmixer using a masterbatch approach. Compounding conditions, i.e., speed and time, were varied to achieve a Hegman grind of 5 in the masterbatch. A series of silica loading was achieved by letting back or diluting each masterbatch. Rheological evaluation was performed using a TA Instruments AR2000 controlled stress rheometer using 4 cm parallel plates; all measurements were performed at 25ºC.
3 "Polyester Polyols Show Advantages in Polyurethane Adhesives," www.specialchem4adhesives.com
4 "Poly bd Resins In Adhesive Applications," Sartomer Application Bulletin, www.sartomer.com
5 "Creating Bio-based Polyols for Adhesives Sealants," Dow Renuva Product Brochure, www.dow.com

Summary

Good thickeners are needed to match the viscosity of each component of the PUR so that uniform mixing and consistent application of the adhesive system is achieved. High ease of dispersion enables formulators to reduce processing time and cost. Clarity is important to formulators working in unfilled systems but may also be useful to all formulators as a general indicator of air or bubble release.

Table 1: CAB-O-SIL® treated fumed silica selector guide for polyols

	Type of Polyol	Polyether	Polyester	Polybutadiene	Soy
	Cabot Fumed Silica Products				
Performance/Properties	Most thickening	TS-720	TS-720 TS-530	TS-720	TS-720
	Easy dispersion	TS-610	TS-610	TS-610	TS-610
	Highest clarity	TS-720	-	TS-610 TS-530	TS-610 TS-530

Products in red: best performance
Products in black: also suitable

Materials & methods

The polyols listed in Table 2 below are primarily difunctional alcohols commonly used in PUR adhesives. The polymer repeat unit is different for each case. A relevant selection of Cabot's commercial portfolio of fumed silica additives was used. As shown in Table 3, the properties of the fumed silicas evaluated clearly exhibit a wide range of characteristics.

Table 2: Overview of polyol characteristics

TYPE	Product name	Vendor	MW (g/mole)	Avg hydroxyl value (mg KOH/g)	RT viscosity(cP)	Functionality
Polyether - Poly (propylene glycol)	Voranol™ 220-056[6]	Dow Chemical	2000	56	300	2
Polyester - diethylene glycol adipate	Diexter® G 1100-56[7]	COIM	2000	56	7500	2
Polybutadiene	Poly bd® R45 HTLO[8]	Sartomer	2800	47	8000	2.5
Soy	Soyol™ R2-052G[9]	Urethane Soy Systems	-	55	1000	2

In this guide, effective thickening is expressed as a relative viscosity. By definition, it is the viscosity of the compounded system that is normalized by the viscosity of the base material. For this case, the base is one of the as-received polyols listed in Table 2.
Ease of dispersion is defined as total time to grind the masterbatch to a Hegman grind of 5. Clarity of each masterbatch was qualitatively assessed for translucency or transparency.

Table 3: Overview of CAB-O-SIL fumed silica products

CAB-O-SIL product	Surface treatment	Level of treatment	Nominal BET surface area of base silica (m^2/g)
M-5	None	None	200
TS-610	Dimethyldichlorosilane	Intermediate	130
TS-530	Hexamethyldisilazane	High	320
TS-720	Polydimethylsiloxane	High	200

[6] Voranol is a trademark of The Dow Chemical Company
[7] Diexter is a registered trademark of COIM
[8] Poly bd is a registered trademark of Sartomer
[9] Soyol is a trademark of Urethane Soy Systems Company

Cabot: A Proud History and Global Reach

Cabot Corporation is a global performance materials company, and we strive to be our customers' partner of choice. We have been a leading manufacturer for more than 130 years. Our global reach enables us to partner closely with our customers to meet the highest standards for performance, quality, and service.

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