TEST METHOD

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Supersedes: DOWM 101212-ME97C

Viscosity of Formulations containing B-Staged Divinylsiloxane-bis(benzocyclobutene)

1. Scope

1.1 This method is applicable to the determination of the viscosity of formulations containing B-staged divinylsiloxane-bis(benzocyclobutene) (B-staged DVS-bis-BCB; CAS #124221-30-3) and mesitylene (CAS #000108-67-8) over a range of 8 to 2000 centistokes (cSt).

Note: B-staged DVS-bis-BCB is a pre-polymer prepared from a mixture of isomers of 1,3-bis(2-bicyclo[4.2.0]octa-1,3,5-triene-3-ylethenyl)-1,1,3,3-tetramethyl-disiloxane.

2. Principle

2.1 The viscosity of the sample is determined using a Brinkmann Lauda Viscotimer C with Ubbelohde viscometers or SVM3000 Stabinger Viscometer.

3. Safety

3.1 Each analyst must be acquainted with the potential hazards of the equipment, reagents, products, solvents and procedures before beginning laboratory work. SOURCES OF INFORMATION INCLUDE: OPERATION MANUALS, MATERIAL SAFETY DATA SHEETS, LITERATURE AND OTHER RELATED DATA. Safety information should be requested from the supplier. Disposal of waste materials, reagents, reactants and solvents must be in compliance with applicable governmental and company requirements.

4. Interferences

4.1 No direct interferences have been observed in the use of this method. If results are suspect based on the analytical history of the product, the data should be confirmed by an alternate method.

5. Apparatus

5.1 Viscometer: Lauda Viscotimer C, available from Brinkmann Instruments, Inc., 1 Cantiague Road, PO Box 1019, Westbury, NY 11590-0207, or equivalent.

5.2 Ubbelohde viscometers: capillary numbers II, IIC, III, IIIC and IV, available from Schott America, 3 Odell Plaza, Yonkers, NY 10701, or equivalent.

5.3 Viscoboy 2 program: also known as the Brinkmann Viscotimer C program, available from Brinkmann Instruments, Inc., or equivalent.

5.4 Computer: Epson HX-20 calculator and KM2 interface, available from Brinkmann Instruments, Inc., or equivalent.

5.5 Bath and circulator: polycarbonate viscosity bath with a Lauda MS constant temperature circulator, available from Brinkmann Instruments, Inc., or equivalent.

5.6 Mechanical pipet: capable of delivering 25-mL aliquots, Oxford Benchmate pipet, with disposable tips, available from Fisher Scientific, 711 Forbes Avenue, Pittsburgh, PA 15219, or equivalent.

5.7 Thermometer: Fluke 2180A RTD digital thermometer, available from John Fluke Mfg. Co. Inc., PO Box 9090, Everett, WA 98206, or equivalent.

5.8 SVM3000 Stabinger Viscometer: Anton Paar USA Inc 10215 Timber Ridge Dr., Ashland, VA 23005, or equivalent.

6. Reagents

6.1 Silicone oil standards: RT10, RT50, RT100, RT500, and RT1000, available from Cannon Instrument Company, PO Box 16, State College, PA 16804-0016, or equivalent.

6.2 Tetrahydrofuran: available from the Fisher Scientific, or equivalent.

6.3 Acetone: available from the Fisher Scientific, or equivalent.

6.4 Nitrogen: available from Scott Specialty Gases, Inc., 6141 Route 611, Plumsteadville, PA 18949, or equivalent.

7. Calibration - Lauda Viscotimer C with Ubbelohde Viscometer

7.1 Turn on the bath and circulator (Section 5.5) and wait until the temperature equilibrates to 25.00 ± 0.02 °C.

7.2 Check to make sure the water level is approximately one inch below the top of the bath.

7.3 Select the appropriate Ubbelohde viscometer (Section 5.2) based on the expected viscosity:

Expected Viscosity	**Ubbelohde Viscometer Capillary #**	**Recommended Silicon Oil Standard**
(cSt)		
9 - 25	II	RT 10 or RT50
27 - 60	IIC	RT 50 or RT100
90 - 200	III	RT 100 or RT 500
270 - 600	IIIC	RT 500 or RT1000
900 - 2000	IV	RT 1000

Note: During the accuracy study, the standard oils used often resulted in efflux times which exceeded 250 seconds. This is not recommended for day-to-day analyses because the optical sensors can be inadvertently tripped by floating particles or bubbles in the constant temperature bath resulting in erroneous efflux times. For the capillary viscometers used with this method, it is recommended that a standard oil which gives an efflux time between 90 and 200 seconds be used.

7.4 Insert the Ubbelohde viscometer into the stainless steel holder

Note: The shape of the viscometer ensures that it can only be inserted one way in the holder).

7.5 Secure the viscometer into the holder by clipping the wire spring at the bottom to the holder under the locking device.

7.6 With the viscometer secured, use a mechanical pipet (Note 14.1) to deliver approximately 25 mL of the appropriate silicone oil standard (Section 7.3) to the viscometer. Fill until the liquid level is between the fill lines on the side of the viscometer. Try to minimize the number of air bubbles in the viscometer.

7.7 Place the holder into the bath. Be sure not to get any water into the viscometer.

7.8 If using a Brinkmann Lauda Viscotimer unit with the Viscoboy 2 program, follow the instructions given in Sections 7.9 to 7.14. If using a unit from a different manufacturer, consult the accompanying manual for instruction on how to set-up and run that system.

7.9 To insert the viscometer into the measurement stand, proceed as follows:

7.9.1 Align the slot on the base of the holder so that it points to the front.

7.9.2 Lift the centering slide on the measurement stand to the top position. Place the base of the holder on the foot of the measurement stand.

7.9.3 Align the slot on the base of the holder with the knob on the foot of the measurement stand. Gently move the viscometer upright so that the measurement bulb sits in between the optical sensors of the measurement stand. The base should lock into place to prevent the viscometer from moving out of position.

7.9.4 Once the viscometer is sitting vertically, lower the centering slide. This will center the entire unit.

7.10 Connect the pressure tubing to the fill tube on the viscometer and connect the venting tubing to the vent tube on the viscometer. The two tubes are different diameters and are not interchangeable.

7.11 Turn on the computer and printer. Load the Viscoboy 2 program according to the instructions outlined in the manual (Section 15.1).

7.12 Once the program has been loaded (Section 7.11), enter the Viscoboy 2 program by following the instructions outlined in the manual (Section 15.1) and initialize the system. The constants to be used are as follows:

User:	0
Therm. Measur:	3
Solvent Visc:	0
Concentration:	1
St. Dev. Tol:	1
Hag. Corr. Limit:	0

7.13 Type 'S' at the main menu to start data collection. Enter the information as prompted by the program. The following parameters were used for this testing:

When Prompted	Enter
Number of Measurements Required:	5
Interval Between Measurements (min):	0

7.14 Once the parameters have been entered (Section 7.13), the program will start the viscosity measurements. The raw times will be printed as the program proceeds. At the end of the measurements, the average time (seconds), the standard deviation of the times, and the kinematic viscosity will all be calculated and printed.

7.15 If unit is equipped with an automated cleaning assembly, follow the instruction provided with the unit to clean the viscometer. Otherwise, follow the instructions given in Sections 7.16 - 7.17.

7.16 Disconnect the pressure and venting tubing from the viscometer and remove the viscometer from the bath.

7.17 Clean out the viscometer with tetrahydrofuran (Section 6.2) followed by an acetone rinse (Section 6.3). Be sure to secure the viscometer before cleaning.

8. Calibration - Stabinger Viscometer

8.1 Turn on the bath and circulator (Section 5.5) and wait until the temperature equilibrates to 25 °C. Press "Menu" button for the air density reading, it should be less than 0.0014 g/cm^3.

8.2 Use a 5 mL disposable syringe with a luer slip tip and draw one volume of the appropriate silicon oil standard as indicated in Section 7.3. Try to minimize the number of air bubbles in the viscometer.

8.3 Remove the air hose from the stainless steel filling port located near the top, front right-hand side of the viscometer. Make sure the tip of the syringe is wiped clean, then connect the syringe to the filling port firmly and securely to ensure no sample will ooze out during filling.

8.4 Press MENU to make the display indicate "Filling" mode.

8.5 Push the syringe plunger very slowly with the minimum amount of pressure necessary to inject the standard into the port. Continue injecting while watching the standard in the waste line until you see no more bubbles emerging (approximately 2-3 mL).

8.6 Press START. The display arrow will change to "Measuring". Gently push another 0.5 mL into the port watching for bubbles in the waste line.

8.7 Re-measure the standard silicone oil twice more by injecting more (pushing the old aliquot out with 1-2 mL of the new one) and pressing START again.

8.8 Report the average of the three kinematic viscosity (ny) measurements

8.9 Clean the instrument first with a syringe full of air, then with 3 volumes of 20 mL of THF, and 5 mL of acetone to confirm all polymer has been removed (turns white when exposed to acetone), and 10 mL THF.

8.10 Reconnect the viscometer's air hose to the sample port. Press PUMP to start the built-in air pump. It will take about 2-3 minutes to dry the cell. Monitor the density reading ("raw") on the display until it reads less than 0.0014 g/cm^3 and then turn the pump off.

9. Procedure - Lauda Viscotimer C with Ubbelohde Viscometer

9.1 Use a mechanical pipet to transfer approximately 25 mL of the sample into the Ubbelohde viscometer. Fill until the liquid level is between the fill lines on the side of the viscometer. Try to minimize the number of air bubbles in the viscometer.

9.2 Repeat Sections 7.7 to 7.17 to determine the viscosity (cSt) of the sample.

10. Procedure - Stabinger Viscometer

10.1 Use a 5 mL disposable syringe with a luer slip tip and draw one volume of the sample. Try to minimize the number of air bubbles in the viscometer.

10.2 Repeat Sections 8.3 to 8.10 to determine the viscosity (cSt) of the sample.

11. Precision

11.1 Lauda Viscotimer C with Ubbelohde Viscometer

11.1.1 Precision data determined from multiple analyses [n] of four different formulations are given below. The analyses were performed over a two-day period.

11.1.2 At the 95% confidence level, individual measurements on similar samples may vary from the long-term average by the values shown below [$\pm t_{(n-1)} \times s$; where $t_{(n-1)}$ = t-value at n-1 degrees of freedom, and s = standard deviation of the validation data]. This assumes a normal distribution of results and equal variability between locations.

Sample	**n**	**$t_{(n-1)}$**	**Average**	**Standard Deviation**	**Relative Standard Deviation**	**At the 95% confidence level, individual measurements may vary from the long-term average by:**
			(cSt)	*(cSt)*	*(%)*	*(± cSt)*
1	6	2.57	15.08	0.010	0.066	0.026
2	6	2.57	50.97	0.16	0.31	0.41
3	6	2.57	245.42	0.58	0.23	1.5
4 (Note 14.3)	6	2.57	963.86	1.82	0.19	4.6

11.2 Stabinger Viscometer

11.2.1 Precision data determined from multiple analyses [n] of three different formulations are given below. The analyses were performed over a two-day period.

11.2.2 At the 95% confidence level, individual measurements on similar samples may vary from the long-term average by the values shown below [$\pm t_{(n-1)} \times s$; where $t_{(n-1)}$ = t-value at n-1 degrees of freedom, and s = standard deviation of the validation data]. This assumes a normal distribution of results and equal variability between locations.

Sample	n	$t_{(n-1)}$	Average	Standard Deviation	Relative Standard Deviation	At the 95% confidence level, individual measurements may vary from the long-term average by:
			(cSt)	*(cSt)*	*(%)*	*(± cSt)*
1	6	2.57	6.18	0.17	2.69	0.4
2	6	2.57	50.88	0.035	0.07	0.1
3	6	2.57	1105.36	4.26	0.39	11.0

12. Accuracy (Note 10.2)

12.1 Lauda Viscotimer C with Ubbelohde Viscometer

12.1.1 Analysis of Cannon silicone oil standards with viscosities ranging from 48 to 990 cSt gave the following results:

Cannon silicone oil standards	Capillary #	Theoretical Viscosity	Observed Viscosity	Difference	Allowable Deviation
		(cSt)	*(cSt)*	*(%)*	*(± %)*
RT50	II	48.44	48.53	0.19	0.3
RT100	IIC	100.13	100.38	0.25	0.3
RT100	III	100.13	100.22	0.09	0.3
RT500	III	514.65	515.08	0.08	0.3
RT1000	IIIC	990.63	990.16	-0.05	0.3

12.2 Stabinger Viscometer

12.2.1 Analysis of Cannon silicone oil standards with viscosities ranging from 48 to 990 cSt gave the following results:

Cannon silicone oil standards	Theoretical Viscosity	Observed Viscosity	Difference	Allowable Deviation
	(cSt)	*(cSt)*	*(%)*	*(± %)*
RT50	49.11	49.12	0.02	0.3
N140	297.0	297.07	0.02	0.5
RT1000	1007	1012.7	0.56	1.0

13. Correlation

13.1 The performance of Ubbelohde technique has been compared to the performance of the Stabinger Viscometer.

13.2 Precision data determined from multiple analyses [n] of 9 formulation samples are given below. The observed F ratio (the larger variance [s^2, where s = standard deviation] divided by the smaller variance) is below the critical F value at the 95% confidence level, so there is no reason to assume that the methods have different precision.

Product	Method	n	Degrees of Freedom	Average	Standard Deviation	F ratio	Critical $F_{(df=7,7)}$
				(cSt)	*(cSt)*		
3022-35	Ubbelohde	8	7	14.23	0.065	2.195	4.995
	Stabinger	8	7	14.13	0.096		
3022-46	Ubbelohde	30	29	51.54	0.399	1.427	2.101
	Stabinger	30	29	54.58	0.477		
3022-57	Ubbelohde	8	7	255.2	0.999	3.995	4.995
	Stabinger	8	7	256.7	1.987		
3022-63	Ubbelohde	4	3	893.0	38.118	1.158	15.439
	Stabinger	4	3	885.0	35.429		
4022-25	Ubbelohde	24	23	36.3	0.459	1.392	2.312
	Stabinger	24	23	36.1	0.389		
4022-35	Ubbelohde	10	9	191.1	1.594	1.228	4.026
	Stabinger	10	9	191.1	1.438		
4024-40	Ubbelohde	10	9	348.1	1.893	1.820	4.026
	Stabinger	10	9	346.8	2.554		
4026-46	Ubbelohde	30	29	1100.2	19.538	1.563	2.101
	Stabinger	30	29	1089.1	15.628		
P6001	Ubbelohde	20	19	6.2	0.145	1.060	2.526
	Stabinger	20	19	6.2	0.141		

13.3 Accuracy data determined from multiple analyses [m] of nine formulation samples of are summarized below. For each sample the difference [d = (Ubbelohde) - (Stabinger)] was calculated. The average difference [$\bar{d}$] between both methods was examined with a paired t-test [$t_{paired} = \bar{d} \times \sqrt{m} / s_d$ where s_d = the standard deviation of d]. For five of the products the observed t-value (t_{paired}) is below the critical t-value at the 95% confidence level, so there is no reason to assume any bias between the Stabinger viscometer and the Ubbelohde technique. Bias was detected between the Stabinger measurement and the Ubbelohde Tube viscosity measurements for 3022-35, 3022-63, 4026-46, and P6001 (Note 14.4).

Product	m	df	Range of Differences	Standard Deviation of the Differences	Average Difference	t_{paired}	Critical $t_{(df)}$
			(%)	*(%)*	*(cSt)*		
3022-35	8	7	0.7	0.04	0.1	5.95	2.57
3022-46	30	29	-0.1	0.18	-0.04	1.23	2.05
3022-57	8	7	-0.6	2.33	-1.51	1.84	2.36
3022-63	4	3	0.9	3.31	7.95	4.81	3.18
4022-25	24	23	0.7	0.20	0.25	6.21	2.07
4022-35	10	9	0.0	0.82	0.01	0.03	2.26
4024-40	10	9	0.4	1.85	1.25	2.14	2.26
4026-46	30	29	1.0	14.17	11.07	4.28	2.05
P6001	20	19	0.3	0.01	0.02	9.26	2.09

14. Notes

14.1 For standards and samples with higher viscosities, it may be necessary to enlarge the opening of the pipet disposable tip by carefully cutting off a small portion of the tip.

14.2 Analytical method performance can be affected by minor differences in instrumentation, reagents, and laboratory technique. Consequently, the method should be qualified in the performing laboratory to confirm its performance and suitability. In addition, analytical instruments should be calibrated at appropriate frequencies.

14.3 During the precision study, formulation #4 was tested only in an Ubbelohde viscometer with a #IIIC capillary. An Ubbelohde viscometer with a #IV capillary could be used to decrease the efflux time, however, precision or accuracy data were not obtained with this capillary size. Both precision and accuracy values should be obtained if a viscometer with a #IV capillary is to be used for samples like formulation #4.

14.4 Bias was detected between the Stabinger measurement and the Ubbelohde Tube viscosity measurements for 3022-35, P6001, 3022-63, and 4026-46. The bias for 3022-35 and P6001 was deemed insignificant to with regards to the specification range. The bias for 3022-63 and 4026-46 was observed as a result of the time necessary to complete the Ubbelohde Tube viscosity measurement increasing over time.

15. References

15.1 "Operating Instructions for the Lauda Viscoboy 2 and Control/Evaluation Unit with Coupler Module KM2", BAV2 KM2-E 11/86, Brinkmann Instruments, Inc.

15.2 "Operating Instructions for the Lauda Viscotimer C", series G 03001 9/86, Brinkmann Instruments, Inc.

15.3 "Service Manual SVM 3000 / G2", C18IB14-A.fm August 2005, Anton Paar, GMBH.