SPRINGER LABORATORY

Springer Laboratory Manuals in Polymer Science

Pasch, Trathnigg: HPLC of Polymers ISBN: 3-540-61689-9 (hardcover) ISBN: 3-540-65551-4 (softcover)

Mori, Barth: Size Exclusion Chromatography

ISBN: 3-540-65635-9

Pasch, Schrepp: MALDI-TOF Mass Spectrometry of Synthetic Polymers

ISBN: 3-540-44259-6

Kulicke, Clasen: Viscosimetry of Polymers and Polyelectrolytes

ISBN: 3-540-40760-X

Hatada, Kitayama: NMR Spectroscopy of Polymers

ISBN: 3-540-40220-9

Brummer, R.: Rheology Essentials of Cosmetics and Food Emulsions

ISBN: 3-540-25553-2

Mächtle, W.; Börger, L.: Analytical Ultracentrifugation of Polymers and

Nanoparticles

ISBN: 3-540-23432-2

Rheology Essentials of Cosmetic and Food Emulsions

184 Figures, 139 in color and 18 Tables



Rüdiger Brummer Beiersdorf AG Unnastr. 48 20245 Hamburg Germany e-mail: Ruediger.Brummer@Beiersdorf.com

Library of Congress Control Number: 2005930321

ISBN-10 3-540-25553-2 **Springer Berlin Heidelberg New York** ISBN-13 978-3-540-25553-6 **Springer Berlin Heidelberg New York**

This work is subject to copyright. All rights are reserved, whether the whole or part of the material is concerned, specifically the rights of translation, reprinting, reuse of illustrations, recitation, broadcasting, reproduction on microfilm or in any other way, and storage in data banks. Duplication of this publication or parts thereof is permitted only under the provisions of the German Copyright Law of September 9, 1965, in its current version, and permissions for use must always be obtained from Springer. Violations are liable for prosecution under the German Copyright Law.

Springer is a part of Springer Science+Business Media springeronline.com

© Springer-Verlag Berlin Heidelberg 2006 Printed in Germany

The use of general descriptive names, registered names, trademarks, etc. in this publication does not imply, even in the absence of a specific statement, that such names are exempt from the relevant protective laws and regulations and therefore free for general use.

Cover design: KünkelLopka GmbH, Heidelberg; design&production, Heidelberg, Germany Typesetting and production: LE-TEX Jelonek, Schmidt & Vöckler GbR, Leipzig, Germany

2/3141 YL 5 4 3 2 10 - Printed on acid-free paper

Springer Laboratory Manuals in Polymer Science

Editors

Prof. Howard G. Barth DuPont Company P.O. box 80228 Wilmington, DE 19880-0228 USA e-mail: Howard.G.Barth@usa.dupont.com

Priv.-Doz. Dr. Harald Pasch Deutsches Kunststoff-Institut Abt. Analytik Schloßgartenstr. 6 64289 Darmstadt Germany e-mail: hpasch@dki.tu-darmstadt.de

Editorial Board

PD Dr. Ingo Alig Deutsches Kunststoff-Institut Abt. Physik Schloßgartenstr. 6 64289 Darmstadt Germany email: ialig@dki.tu-darmstadt.de

Prof. Josef Janca Université de La Rochelle Pole Sciences et Technologie Avenue Michel Crépeau 17042 La rochelle Cedex 01 France email: jjanca@univ.lr.fr

Prof. W.-M. Kulicke
Inst. f. Technische u. Makromol. Chemie
Universität Hamburg
Bundesstr. 45
20146 Hamburg
Germany
email: kulicke@chemie.uni-hamburg.de

Prof. H. W. Siesler Physikalische Chemie Universität Essen Schützenbahn 70 45117 Essen Germany

email: hw.siesler@uni-essen.de

About the Author

Rüdiger Brummer is a physicist at Beiersdorf AG with research interests in pressure-sensitive adhesives and cosmetic emulsions. He has published several professional papers and is the holder of patents. He completed his physics degree at the Christian Albrecht University in Kiel. Beginning in 1978 he worked as a scientist in the basic research laboratory of the Dr. Beyschlag Company in Heide.

In 1981 he moved to Phoenix AG in Hamburg, where he worked in a development laboratory for metal-rubber materials and started programming with finite elements. After several years he joined Beiersdorf AG, where he started with rheological



measurements. In 1991 he became head of the Rheology and Thermal Analysis Department at Beiersdorf AG in Hamburg.

Rüdiger Brummer is a member of the German Rheology Society and the American Society of Rheology. He is active in the German DIN for viscosity and in the IUPAC sub-committee Structure and Properties of Commercial Polymers.

Dedication

Dedicated to my paternal friend and physicist colleague **Dr. Gustav Richter**

Konfuzius (551–479 BC) Humans have three ways to act intelligently: First of all: by thinking – that is the noblest. Secondly: by copying – that is the easiest. Thirdly: by experience – that is the bitterest.

Foreword

In the last decade, technical progress has positively influenced the methods of dynamic mechanical analysis. At the same time, data handling has become more comfortable and much easier.

In this context it is not at all surprising that various techniques of rheology have opened up new insights into so far unknown and undiscovered structures.

Furthermore, new correlations between rheological behavior and specific product or structure properties have been revealed and are used for systematic investigations.

However, sound information about the proper use of rheological techniques is still weak. The majority of published information deals with the rheology of polymers. This book focuses on the rheology of dispersions and emulsions. Students, chemists, engineers and laboratory assistants working on these materials, will find in this book fundamental principles, how to apply rheology, and what kind of information can be obtained.

I wish all readers a lot of energy and enthusiasm for the opportunities offered by rheological techniques.

May 2005

Prof. Dr. Klaus-Peter Wittern Corporate Vice President University of Hamburg, Department of Chemistry

Preface

In the last 20 years, personal computers have become more and more powerful. As a result, dynamic mechanical analysis (DMA) has become more and more efficient and rheology has consequently become a common tool in the analytical laboratory. Modern rheometers today are three times cheaper than 10 years ago but four times better in performance. Now this technique and the powerful PC are more often employed by the non-specialist.

However, information on the use of this technique is still thinly scattered. There are several excellent books about rheology and many papers covering correlation with other techniques. Most of these describe polymers and only a few books refer to dispersions and emulsions. Still today you often hear the question: "What is DMA and what can it tell me about my product or process?"

This book attempts to give students, chemists, engineers, and laboratory assistants in the cosmetic field a starting point to understand where and how rheology can be applied. Therefore I have minimized the mathematics and statistics and have given information on how to use a rheometer. Rheology is an efficient tool for getting information on material behavior under different conditions and it can be done very cost effectively when done properly.

Hamburg, May 2005

Rüdiger Brummer

Acknowledgements

I have so many people to thank for their help and support; more than I can list here. First of all, I would like to thank Prof. Kulicke for his suggestion and Prof. Wittern for his encouragement to write this book. They gave me the motivation for this project.

Special appreciation is expressed to my colleagues in the Rheology and Thermo Analysis Laboratory – Frank Hetzel, Martin Griebenow, Rüdiger Uhlmann, Volker Schlesiger and Angelika Wiese – for their collaboration and careful preparation of all the test specimens, since all measurements were done in our laboratory.

I would also like to thank all the students who finished their studies in my laboratory, especially Dr. Thorsten Berg, Dr. Sybille Friedrich and Dipl. Ing. Mandy Mühl, for their dedication and the results of their work, some of which I was able to use in this book.

For the micrographs I would like to thank Dr. Roger Wepf and his coworkers at Beiersdorf. All other figures were taken from the manual of the rheometer supplier, or from internet portals, or are my own.

Finding the best English words was the task of Dr. Marcia Franzen-Hintze, who showed a great propensity to understand my point of view on rheology.

I am also grateful to Prof. Werner-Michael Kulicke and Dr. Christian Clasen, who were kind enough to review this manuscript.

Special thanks go to my friend and fellow rheologist, Dr. Bernhard Hochstein, for stimulating discussions while interpreting the data and for his help in reviewing the formulas.

Last but not least, I would like to thank my family and especially my wife, who was so tolerant and understanding while I was writing, revising and correcting this book on holidays, weekends, evenings, etc.

Hamburg, May 2005

Rüdiger Brummer

List of Symbols

$\begin{array}{cccccccccccccccccccccccccccccccccccc$	A	Space	m^2
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	b	Mean droplet diameter	m
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	С	Concentration	$moll^{-1}$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C_1, C_2	Coefficient	_
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	d	Diameter	m
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$d_{\rm v,10}$	10% of the volume diameter	m
E_A Activation energy $J mol^{-1}$ E/m Energy input $J k g^{-1}$ F ForceN G_E Modulus of an ideal elastic solidPa G^* Complex modulusPa G' Storage modulusPa G' Loss modulusPa G_p Plateau modulusPa $G_{1 rad/s}$ Storage modulus at $\omega = 1 rad/s$ Pa h Thicknessm I CurrentA L Lengthm M Molecular weightg mol^{-1} M_{cp} Torque for cone platesN m^{-1} M_{pp} Torque for parallel platesN m^{-1} n Revolutions per minuterpm p PressurePa p_1 Intake pressurePa p Outtake pressurePa p Outtake pressurePa Q Volume per timem R Radiusm R Radiusm R Radiusm t Times t Temperature°C		50% of the volume diameter	m
E/m Energy input $J k g^{-1}$ F ForceN G_E Modulus of an ideal elastic solidPa G^* Complex modulusPa G' Storage modulusPa G' Loss modulusPa G_p Plateau modulusPa $G_{1 rad/s}$ Storage modulus at $\omega = 1 rad/s$ Pa h Thicknessm I CurrentA L Lengthm M Molecular weightg mol^{-1} M_{cp} Torque for cone platesN m^{-1} M_{pp} Torque for parallel platesN m^{-1} n Revolutions per minuterpm p PressurePa p_1 Intake pressurePa p_2 Outtake pressurePa Q Volume per timem³ s^{-1} R Radiusm Re Reynold number- r Radiusm t Times t Temperature° C	$d_{\rm v,90}$	90% of the volume diameter	m
F ForceN $G_{\rm E}$ Modulus of an ideal elastic solidPa G^* Complex modulusPa G' Storage modulusPa G' Loss modulusPa $G_{\rm P}$ Plateau modulusPa $G_{\rm 1rad/s}$ Storage modulus at $\omega = 1{\rm rad/s}$ Pa h Thicknessm I CurrentA L Lengthm M Molecular weightg mol^{-1} $M_{\rm cp}$ Torque for cone platesN m^{-1} $M_{\rm pp}$ Torque for parallel platesN m^{-1} n Revolutions per minuterpm p PressurePa p_1 Intake pressurePa p_2 Outtake pressurePa Q Volume per timem³ s s^{-1} R Radiusm Re Reynold number- r Radiusm t Times t Temperature° C	$E_{\rm A}$	Activation energy	$J mol^{-1}$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	E/m	Energy input	$J kg^{-1}$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	F	Force	N
G' Storage modulusPa G'' Loss modulusPa G_p Plateau modulusPa $G_{1 rad/s}$ Storage modulus at $\omega = 1 rad/s$ Pa h Thicknessm I CurrentA L Lengthm M Molecular weightg mol $^{-1}$ M_{cp} Torque for cone platesN m $^{-1}$ M_{pp} Torque for parallel platesN m $^{-1}$ n Revolutions per minuterpm p PressurePa p_1 Intake pressurePa p Outtake pressurePa Q Volume per timem 3 s $^{-1}$ R Radiusm Re Reynold number- r Radiusm t Times t Temperature° C	$G_{\rm E}$	Modulus of an ideal elastic solid	Pa
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	G^*	Complex modulus	Pa
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	G'	Storage modulus	Pa
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	G''	Loss modulus	Pa
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	G_{p}	Plateau modulus	Pa
h Thicknessm I CurrentA L Lengthm M Molecular weight $g mol^{-1}$ M_{cp} Torque for cone plates $N m^{-1}$ M_{pp} Torque for parallel plates $N m^{-1}$ n Revolutions per minuterpm p PressurePa p_1 Intake pressurePa p_2 Outtake pressurePa Q Volume per time $m^3 s^{-1}$ R Radiusm Re Reynold number- r Radiusm t Times t Temperature°C		Storage modulus at $\omega = 1 \text{rad/s}$	Pa
L Lengthm M Molecular weight $g mol^{-1}$ M_{cp} Torque for cone plates $N m^{-1}$ M_{pp} Torque for parallel plates $N m^{-1}$ n Revolutions per minuterpm p PressurePa p_1 Intake pressurePa p_2 Outtake pressurePa Q Volume per time $m^3 s^{-1}$ R Radiusm Re Reynold number- r Radiusm t Times t Temperature°C		Thickness	m
M Molecular weight $g \mathrm{mol}^{-1}$ M_{cp} Torque for cone plates $N \mathrm{m}^{-1}$ M_{pp} Torque for parallel plates $N \mathrm{m}^{-1}$ n Revolutions per minuterpm p PressurePa p_1 Intake pressurePa p_2 Outtake pressurePa Q Volume per time $\mathrm{m}^3 \mathrm{s}^{-1}$ R Radiusm Re Reynold number- r Radiusm t Times t Temperature° C	I	Current	A
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	L	Length	
$M_{\rm pp}$ Torque for parallel platesN m^{-1} n Revolutions per minuterpm p PressurePa p_1 Intake pressurePa p_2 Outtake pressurePa Q Volume per time $m^3 s^{-1}$ R Radiusm Re Reynold number- r Radiusm t Times t Temperature° C	M	Molecular weight	$g mol^{-1}$
n Revolutions per minuterpm p PressurePa p_1 Intake pressurePa p_2 Outtake pressurePa Q Volume per time $m^3 s^{-1}$ R Radiusm Re Reynold number- r Radiusm t Times t Temperature°C	$M_{ m cp}$	Torque for cone plates	
p PressurePa p_1 Intake pressurePa p_2 Outtake pressurePa Q Volume per time $m^3 s^{-1}$ R Radiusm Re Reynold number- r Radiusm t Times T Temperature°C	$M_{ m pp}$	Torque for parallel plates	$N m^{-1}$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	n	Revolutions per minute	rpm
p_2 Outtake pressurePa Q Volume per time $m^3 s^{-1}$ R Radius m Re Reynold number $ r$ Radius m t Time s T Temperature $^{\circ}$ C	P	Pressure	Pa
$\begin{array}{ccccc} Q & \text{Volume per time} & \text{m}^3 \text{s}^{-1} \\ R & \text{Radius} & \text{m} \\ Re & \text{Reynold number} & - \\ r & \text{Radius} & \text{m} \\ t & \text{Time} & \text{s} \\ T & \text{Temperature} & & ^{\circ}\text{C} \end{array}$	p_1	Intake pressure	Pa
R Radiusm Re Reynold number- r Radiusm t Times T Temperature $^{\circ}$ C	p_2	Outtake pressure	
ReReynold number- r Radiusm t Times T Temperature° C			$m^3 s^{-1}$
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	R	Radius	m
$egin{array}{cccc} t & { m Time} & { m s} \\ T & { m Temperature} & { m ^{\circ}C} \end{array}$	Re	Reynold number	_
T Temperature °C	r	Radius	m
1		Time	
T Absolute temperature K		-	
	T	Absolute temperature	K

U	Voltage	V
ν	Speed	$m s^{-1}$
\dot{V}	Volume per time	$m^3 s^{-1}$
w	Characteristic rate	s^{-1}
\overline{x}	Average length	m
β	Angle	0
δ	Phase angle	0
η	Dynamic viscosity	Pas
$\eta_{ m rel}$	Relative viscosity	Pas
λ	Wavelength	m
Q	Density	kgm^3
Y	Deformation	%
Ϋ́	Shear rate	s^{-1}
τ	Shear stress	Pa
$ au_{ m yield}$	Yield stress	Pa
$ au_i$	Relaxation time	s^{-1}
ν	Cinematic viscosity	$m^2 s^{-1}$
ω	Frequency	$rads^{-1}$

List of Abbreviations

American Society for Testing Materials
critical micelle constant
Deutsches Arzneibuch
Deutsche Industrie Norm
International Cosmetic Ingredients Dictionary
International Organization for Standardization
Japanese Standards Association
Nuclear magnetic resonance
Pulsed-field gradient spin echo
Polyglyceryl-2-dipolyhydroxystearate
Reynolds number
Transmission electron microscopy
Polyglyceryl-3-diisostearate
Gesetz gegen den unlauteren Wettbewerb
Lebensmittel- und Bedarfsgegenständegesetz
Heilmittelwerbegesetz
Musterberufsordnung der Deutschen Ärzte

Table of Contents

1	INT	RODUC	TION	1	
2	A TF	RIP BAC	CK IN TIME	5	
3	SKIN	N AND I	TS CARE	15	
4	EMU	JLSION	S – SOME THEORETICAL ASPECTS	17	
	4.1	Physic	ochemical Structure of Cosmetic Products	17	
	4.2	Moder	n Emulsifiers	19	
	4.3		are and Cleansing	19	
	4.4		emulsions	19	
	4.5	Emulsi	ifier-Free Products	20	
	4.6	Produc	ction of Emulsions	21	
	4.7	Proces	ses Occurring During Emulsification	21	
	4.8	Serrate	ed Disc Disperser	22	
5	BASIC PHYSICAL AND MATHEMATICAL PRINCIPLES 2				
	5.1	Import	tant Definitions	25	
	5.2	One-D	imensional Parallel Plates Model	28	
	5.3	Paralle	el Plate Measuring System	30	
	5.4	Cone-I	Plate Measuring System	31	
	5.5		ıl Cylinder Systems	32	
	5.6		e Gap Measuring System	35	
	5.7	Flow T	Through Circular Capillary		
	5.8			38	
		5.8.1	PP Measurement System	39	
		5.8.2	Cylinder Measurement Systems	39	
		5.8.3	Circular Capillaries	39	
	5.9	Deform	nation and Relaxation	40	
	5.10	Thixot	ropy and Rheopexy	43	
	5.11	5.11 Vibration or Oscillation Measurements		44	
		5.11.1	Steady and Dynamic Stress	45	
		5.11.2	Ideal Elastic Solids	46	
		5.11.3	Ideal Viscous Fluids	46	
		5.11.4	Real Solids	47	
		5 11 5	Complex Representation	48	

6	MEA	SURIN	G INSTRUMENTS	51
	6.1	Moder	n Rheometer	52
	6.2	High S	hear Rheometer	54
	6.3	Standa	rd Viscometer	55
	6.4	Often I	Used Viscometer	56
	6.5	Autom	atic Sampler	57
	6.6	In-pro	cess In-/On-line Viscosity Measurements	58
	6.7		Prospects	61
7	MOS	T IMPO	DRTANT TEST METHODS	63
	7.1	Stress	Ramp Test	65
	7.2		nian Flow Behavior	67
	7.3		Test and Creep Recovery	67
	7.4		eal Elastic Behavior	68
	7.5		eal Viscous Behavior	68
	7.6		iscoelastic Behavior	69
	7.7		Flow Curve	69
	7.8		tude Dependence	71
	7.9		are Breakdown and Build Up	73
			Dependence	74
	7.11		ency Test	75
	7.12		rature Dependence	76
			ned Temperature-Time Test	77
			1	
8			OF MEASURING RESULTS AND CORRELATIONS	
			ER TESTS	81
	8.1		tress	81
		8.1.1	Correlations of the Yield Stress with the Primary Skin Feel	
		8.1.2	Optimization of the Stress Ramp Test	83
		8.1.3	Residue Emptying	85
		8.1.4	Energy Input	87
			8.1.4.1 Measurement of the Energy Input	88
		8.1.5	Droplet Sizes and their Distribution	90
		8.1.6	Pumpability of Cosmetic Emulsions	92
			8.1.6.1 Estimation of the Maximum Shear Rate	93
			8.1.6.2 Calculation of the Shear Stress	94
		8.1.7	Stability Studies Using Yield Stress Measurements	95
		8.1.8	Results Obtained	96
	8.2	Steady	Flow	97
		8.2.1	Determination of the Measuring Time	97
		8.2.2	Temperature Dependence of the Dynamic Viscosity	98
		8.2.3	Secondary Skin Feel	99
			8.2.3.1 Investigation of the Secondary Skin Feel	100
	8.3	Oscilla	tory Measurements	101
		8.3.1	Temperature Dependence of the Moduli	106

		8.3.2	Temperature Stability	
		8.3.3	Rheological Swing Test for Temperature Stability	112
	8.4		emperature Superposition (TTS)	117
		8.4.1	Softening Point	118
		8.4.2	Freezing Point	118
		8.4.3	Determination of the Master Curve at Constant Frequency	118
			8.4.3.1 Determination of the Activation Energy	
			via the Temperature	119
			8.4.3.2 Viscosity	119
			8.4.3.3 Arrhenius Equation	120
			8.4.3.4 WLF Equation	122
			8.4.3.5 First Conclusion	122
			8.4.3.6 Determination of the Master Curve	
			with Variable Frequency	123
			8.4.3.7 Final Conclusion	124
9	INTE	ERPRETA	ATION	125
	9.1	Relation	nships for Polymers	125
	9.2	General	Statements for Cosmetic Emulsions	127
10	CAL	BRATIC	DN/VALIDATION	131
			rinciples of Statistical Analysis	133
		10.1.1	Normal Distribution (Gaussian Distribution)	133
		10.1.2	Mean Value	134
		10.1.3	True Value	135
		10.1.4	Standard Deviation and Variance	135
			10.1.4.1 Standard Deviation	136
			10.1.4.2 Coefficient of Variation	136
		10.1.5	Measured Value, Result, Random Variable	136
		10.1.6	Population, Series, Measured Value	137
		10.1.7	Errors and Deviations	137
			10.1.7.1 Error Types	137
		10.1.8	Precision	138
		10.1.9	Accuracy	139
		10.1.10	Trueness	139
		10.1.11	Repeatability	139
			Reproducibility	140
			Outliers	140
	10.2		the Laboratory	140
		10.2.1	Calibration Test for Oscillatory Measurements	143
		10.2.2	Temperature	145

REFERENCES	
	173
chorheology	170
colate	
ms	169
ch	168
zipan	
hurt	
chup	
ese	
dwich Spreads	
ney	
.1 The Origins of Food Rheology	
nort History of Food Rheology	
ON IN THE WORLD OF FOOD RHEOLOGY	161
nments	160
ertising Cosmetic Products	
keting of Cosmetic Products	
ning, Trademark Law, Patents Law	156
duction of Cosmetic Products	155
metics vs. Drugs	155
ION OF COSMETICS	155
rpretation	152
ng of Cone-plate and Parallel Plate Measuring Systems rpretation	150 152
surement Artifacts	
aning Measuring Systems	
nder Systems	
allel Plate	
e-plate	
erials for Geometric Systems	147
D TRICKS	147
TRICKS .	