

Application Handbook Thermal Analysis

热分析应用手册系列丛书

Jürgen E.K. Schawe →

..... 陆立明 →

著
译

弹性体 Elastomers

东华大学出版社

热分析应用手册

Application Handbook

Thermal Analysis

弹性体 Elastomers

Jürgen E.K. Schawe 著

陆立明 译

本应用手册提供各种精选的应用实例。实验是由瑞士梅特勒-托利多热分析实验室采用在每个应用实例中描述的特定仪器十分认真地完成的,并以最新知识为依据对结果进行评估。

然而,这并非意味着读者无需用自己的适合样品的方法、仪器和用途进行亲自测试。由于对实例的效仿和应用是无法控制的,所以我们当然无法承担任何责任。

使用化学品、溶剂和气体时,必须遵循常规安全规范和制造商或供应商提供的使用指南。

This application handbook presents selected application examples. The experiments were conducted with the utmost care using the instruments specified in the description of each application at METTLER TOLEDO Thermal Analysis Lab in Switzerland. The results have been evaluated according to the current state of our knowledge.

This does not however absolve you from personally testing the suitability of the examples for your own methods, instruments and purposes. Since the transfer and use of an application is beyond our control, we cannot of course accept any responsibility.

When chemicals, solvents and gases are used, general safety rules and the instructions given by the manufacturer or supplier must be observed.

图书在版编目(CIP)数据

热分析应用手册·弹性体/(瑞士)肖(Schawe, J. E. K.)

著;陆立明译. —上海:东华大学出版社, 2009. 7

(热分析应用手册系列丛书)

ISBN 978-7-81111-569-7

I. 热... II. ①肖... ②陆... III. ①热分析—手册
②弹性体—热分析—手册 IV. 0657. 7-62

中国版本图书馆 CIP 数据核字(2009)第 069503 号

责任编辑 竺海娟

封面设计 蔡顺兴

弹性体

东华大学出版社出版

上海市延安西路 1882 号

邮政编码:200051 电话:(021)62193056

新华书店上海发行所发行 苏州望电印刷有限公司印刷

开本:889×1194 1/16 印张:16.5 字数:528 千字

2009 年 7 月第 1 版 2009 年 7 月第 1 次印刷

ISBN 978-7-81111-569-7/TS·123

定价:65.00 元

序

热分析是仪器分析的一个重要分支,它对物质的表征发挥着不可替代的作用。热分析历经百年的悠悠岁月,从矿物、金属的热分析兴起,近几十年在分子科学和药物分析等方面唤起了勃勃生机。

我国在 20 世纪 50~60 年代,科研单位、高校和产业部门为满足科研、教学和生产的需要,经历了从原理出发自行设计研制热分析仪器的艰苦创业阶段;30~40 年前,先进的热分析仪器还只是在少数科研单位的测试中心才拥有,而随着我国综合国力的增强和对科研支持力度的加大,现已逐渐成为许多实验室的通用仪器,在科研和生产中起着越加重要的作用。广大相关专业的科技人员为了更好地利用这些设备,迫切需要深入掌握热分析仪器及相关的基础和应用方面的知识。这套热分析应用系列丛书就是在这样的形势下应蕴而生的。

本书的基础数据主要是由瑞士的梅特勒—托利多(Mettler—Toledo)公司提供的,该公司是全球著名的精密仪器制造和经销商。早在 1945 年,就曾以首台单秤盘替代法天平而闻名于世。随后,又将其与加热炉结合,在 1964 年推出了世界上第一台商品化 TGA/DTA 热分析仪器。1968 年又有 TGA/MS 联用仪和差示扫描量热仪(DSC)相继问世。40 余年来,梅特勒—托利多一直是全球热分析仪器的主要供应商之一。现今具有包括 DSC、TGA/DTA、TMA、DMA 等完备的现代热分析仪器。近年取得的新进展有如:多星型热电堆 DSC 2006 年荣获美国 R&D100 奖,该奖项是每年颁发给当年在全球技术领域具有代表性新产品的开发者;2005 年开发的随机多频温度调制 DSC 技术 TOPEM,能在一次实验中测定准稳态比热容,由热流与升温速率的相关性分析分别得到可逆、不可逆热流量和总热流量,以及反应(转变)过程与频率的关系。

《热分析应用手册》是系统介绍热分析在诸多领域应用的一项系统工程,《弹性体》是其中的一个分册。这套丛书汇集梅特勒—托利多公司瑞士总部和梅特勒—托利多(中国)公司科技人员的智慧而潜心编著的。

该分册的主要作者 Jürgen E. K. Schawe 博士,1984 年获得固体物理学博士学位后,先后于德国 Pedagogical University Güstrow 和 University Ulm 工作,从事有关热聚合物热分析等研究工作。1999 加入瑞士梅特勒—托利多公司,在热分析应用研究方面,有深厚的理论基础与丰富的实践经验。译者陆立明先生 1985 年在华东理工大学获得聚合物材料工学硕士,后在上海市合成树脂研究所从事聚合物研究开发工作 12 年(其中 3 年在德国柏林技术大学进修高分子物理)。加入梅特勒—托利多(中国)公司以来一直从事热分析的技术应用和管理工作的。

本书的酝酿和出版正值我国改革开放 30 年,我国在世界的影响全面提升。据称这一时期我国科技人员在国际期刊发表的论文数量提高近 35 倍(从 1981 年的约 2 千篇到 2006 年的约 7 万篇)。本书的一个明显特点是以中英文对照的形式出版,这就为熟悉英语论文的写作方法提供了一种借鉴。

相信这套丛书的出版,将会对我国热分析技术的普及与提高起到重要的推动作用。

刘振海(签字)

2009 年 4 月 28 日 于长春

著者序

本应用手册以大量实例介绍了弹性体的热分析。用于样品测试的主要技术为热重分析(TGA)、差示扫描量热法(DSC)和动态热机械分析(DMA)。在特别情况下,也采用热机械分析(TMA)和联用技术(TGA/气体分析)。

实践中热分析广泛应用于定性分析,但实际上,当进行定量测试和计算时,可大大有助于解释结果并得到最终结论。因此,我们将注意力放在定量热分析并概述进行可靠测量的基本原则,也论及实验条件对测试结果的影响。

除了需要考虑的基本事项,还讨论了许多复杂的分析和关系。

对于这个相当复杂但有意义的领域的专家和新手们,我希望本书叙述的应用将引起他们广泛的兴趣,并激发新的想法。

我要特别感谢拜耳公司(Leverkusen)的 Claus Wrana 博士提供了样品并进行了许多讨论。我也要感谢 Huber and Suhner 公司(Pfäffikon)的 Willi Weber 提供了 4.3.1 节至 4.7.1 节的测试数据和 Uetendorf 的 Christian Krebs 在采购样品方面的帮助。

我还要对我所有瑞士 Schwerzenbach 的梅特勒-托利多同事们的帮助和鼓励表示感谢:首先是 Markus Schubnell 博士(填充 SBR 测试和 MS 测试)、Cyril Darribère(FTIR 测试)、Rudolf Riesen 博士(TMA 测试和有益的讨论)、Georg Widmann 和 Dudley May 博士(校对德文原稿)。还要感谢 Dudley May 博士将德文稿翻译为英文和他的许多有益建议。

Jürgen E. K. Schawe 博士

Preface

This applications booklet provides an introduction to the thermal analysis of elastomers with a large number of practical examples. The main techniques used for sample measurement are thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA). In particular cases, thermomechanical analysis (TMA) and combined techniques (TGA gas analysis) have also been employed.

In practice, thermal analysis is widely used for qualitative analyses. In fact however, the interpretation of the results and the final conclusions that can be drawn are greatly improved when quantitative measurements and evaluations are performed. We have therefore focused our attention on quantitative thermal analysis and outlined the basic principles for performing reliable measurements. The influence of experimental conditions on the measurement results is also covered.

Besides elementary considerations, a number of complex analyses and relationships are discussed.

I hope that the applications described in this book will find wide interest and stimulate new ideas both for experts and for newcomers to this rather complex but immensely interesting field.

I would like to thank Dr. Claus Wrana (Bayer AG, Leverkusen) in particular for making the samples available and for many discussions. I also thank Willi Weber (Huber and Suhner AG, Pfäffikon) for supplying the measurement data for Sections 4.3.1 and 4.7.1 and Christian Krebs (Uetendorf) for assistance in procuring samples.

Furthermore I would like to thank all my colleagues at METTLER TOLEDO, Schwerzenbach, Switzerland for their help and motivation; above all Dr. Markus Schubnell (for measurements on filled SBR and MS measurements), Cyril Darribère (for FTIR measurements), Dr. Rudolf Riesen (for TMA measurements and helpful discussions), Georg Widmann and Dr. Dudley May for proofreading the original German manuscript. I also owe my thanks to Dr. Dudley May for translating the German text into English and for many helpful suggestions.

Dr. Jürgen E. K. Schawe

出版前言

《热分析应用手册系列丛书》是由梅特勒—托利多瑞士热分析实验室专家撰写的系列手册,包括《热分析基础》、《热塑性聚合物》、《热固性树脂》、《弹性体》、《食品》、《药物》、《无机物》、《化学品》和《热重—逸出气体分析》等分册。

本套书既注重实用性,又注重学术性。它们可以作为应用手册查询,也可以作为实验指南,如帮助选择合适的热分析测试技术和方法、制备和处理样品、设定实验参数等。手册中的所有应用实例均经过认真挑选,实验方法经精心设计,测试曲线重复可靠,数据处理严格谨慎、对实验结果的解释和对实验结论的推导科学合理。

本套手册面向所有用到热分析和对热分析感兴趣的教授、科学家、工程师和学生(特别是研究生)及其他科技工作者,适合所有热分析仪器的直接使用者。

本书是《热分析应用手册系列丛书》之《弹性体》分册。

本分册通过大量实例全面深入地介绍和讨论了热分析在聚合物弹性体方面的应用。第1至第3章为热分析方法简介,弹性体的结构、性能和应用;弹性体的基本热效应。第4至第5章介绍了大量的应用实例,包括对结果的详细解释和导出的结论。

与其他分册一样,本书以中英文对照方式出版,读者可以阅读中文,同时可对照原著。无论对热分析工作者,还是热分析学习者,应该都有帮助和裨益。

这里要特别感谢刘振海教授,他仔细审阅了本书全部书稿,并亲自进行修改,使本书的质量得到了很大提高。

东华大学出版社的编辑对本书的出版也付出了辛勤的劳动,在此表示感谢。

译文甚至原著中,有错误之处,恳望读者指正,以便能在再版时改正,不胜感谢。

陆立明

2009年7月,上海

应用一览表 Application list

标题 Title	主题 Topics							方法 Methods				页码 Page
	玻璃化转变 Glass transition	结晶度/结晶 Crystallinity/crystallization	熔融 Melting	硫化 Vulcanization	组分 Composition	计算方法/实验 Evaluation/experimental Calculation/experiment	其他 Others	DSC/ADSC/IsoStep	TGA/TGA-EGA	TMA/DITMA	DMA	
玻璃化转变温度的 DSC 测量 Measurement of the glass transition temperature with DSC	•					•		•				33
玻璃化转变的计算方法 Evaluation possibilities for the glass transition	•					•		•				34
样品预处理对玻璃化转变的影响 Influence of sample pretreatment on the glass transition	•					•		•				39
结晶度的 DSC 测量 DSC investigations on crystallinity		•						•				42
结晶度测定 Determination of crystallinity		•				•		•				44
以硅橡胶为例的冷结晶 Cold crystallization using silicone rubber as an example		•				•		•				46
EPDM 的玻璃化转变和熔融 Glass transition and melting of EPDM	•		•			•		•				48
硫化反应 DSC 测试的比较 Comparison of DSC measurements of vulcanization reaction				•				•				50
转化率曲线的讨论 Discussion of the conversion curve				•		•		•				52
硫化反应的动力学计算方法(非模型动力学) Kinetic evaluation of a vulcanization reaction (Model Free Kinetics)				•		•		•				53
等温硫化动力学的测量 Measurement of isothermal vulcanization kinetics				•		•		•				56
DSC 和 ADSC 测量的比较 Comparison of DSC and ADSC measurements	•	•	•			•		•				60
SBR 弹性体的典型 TGA Typical TGA of an SBR elastomer					•	•			•			64
样品预处理对 TGA 曲线的影响 Influence of sample preparation on TGA curves					•		•		•			66
TGA 曲线的可再现台阶计算 Reproducible step evaluation for TGA curves					•	•			•			68
硅橡胶的膨胀系数 Expansion coefficient of silicone elastomers							•			•		71
DSC 和 DMA 测量的比较 Comparison of DSC and DMA measurements	•	•	•			•					•	74
DMA 曲线的表示 Presentation of DMA curves	•					•					•	76

续表

标题 Title	主题 Topics							方法 Methods				页码 Page
	玻璃化转变 Glass transition	结晶度/结晶 Crystallinity/crystallization	熔融 Melting	硫化 Vulcanization	组分 Composition	计算方法/实验 Evaluation/experimental Calculation/experiment	其他 Others	DSC/ADSC/IsoStep	TGA/TGA-EGA	TMA/DITMA	DMA	
力学行为大幅度变化的测量 Measurement of large changes in mechanical behavior	•		•			•					•	79
模量和柔量 Modulus and compliance	•					•					•	81
玻璃化转变的频率依赖性 The frequency dependence of the glass transition	•					•					•	82
玻璃化转变不同计算方法的比较 Comparison of different possibilities for evaluating the glass transition	•					•					•	85
松弛与频率关系的测量 Measurement of the frequency dependence of relaxation	•						•				•	88
松弛谱的频率依赖性 Temperature dependence of the relaxation spectrum	•						•				•	90
主曲线绘制 Master curve construction	•					•	•				•	93
天然橡胶(NR)的 TGA TGA of natural rubber (NR)					•				•			96
丁腈橡胶(NBR)的 TGA TGA of acrylonitrile-butadiene rubber (NBR)					•				•			98
丁苯橡胶(SBR)的 TGA TGA of styrene-butadiene rubber (SBR)					•				•			100
乙丙三元橡胶(EPDM)的 TGA TGA of ethylene-propylene-diene rubber (EPDM)					•				•			102
氯丁橡胶(CR)的 TGA TGA of chloroprene rubber (CR)					•				•			103
DSC 玻璃化转变的比较 Comparison of glass transitions by DSC	•							•				106
氯丁橡胶(CR)结晶和熔融的测量 Measurements of the crystallization and melting of chloroprene rubber (CR)		•	•					•				108
预处理对 EPDM 熔融的影响 Influence of pretreatment on the melting of EPDM		•	•			•		•				110
不同种类 EPDM 的 DSC 比较 Comparison of different types of EPDM by DSC	•		•					•				113
结晶对 CR 玻璃化转变的影响 Influence of crystallization on the glass transition of CR	•	•						•				115
结晶对硅橡胶玻璃化转变的影响 Influence of crystallization on the glass transition of a silicone elastomer	•	•				•		•				117
聚氨酯 DSC 和 DMA 测量的比较 Comparison of DSC and DMA measurements of polyurethane	•		•					•			•	121

续表

标题 Title	主题 Topics							方法 Methods				页码 Page
	玻璃化转变 Glass transition	结晶度/结晶 Crystallinity/crystallization	熔融 Melting	硫化/Vulcanization	组分 Composition	计算方法/实验 Evaluation/experimental Calculation/experiment	其他 Others	DSC/ADSC/IsoStep	TGA/TGA-EGA	TMA/ DLTMA	DMA	
氯丁橡胶中碳黑的分析 Analysis of carbon black in elastomers based on chloroprene					•	•			•			162
含不同种类碳黑弹性体的分析 Analysis of elastomers with different types of carbon black					•	•			•			164
填充弹性体的 DLTMA DLTMA of filled elastomers					•	•	•			•		167
NR 弹性体剪切模量与振幅关系的测量 Measurement of the amplitude dependence of the shear modulus of NR elastomers					•		•				•	169
氯醚橡胶和卤化丁基橡胶的 TGA TGA of epichlorohydrin and halogenated butyl elastomers					•				•			171
氟橡胶(FPM)的 TGA TGA of fluoroelastomers (FPM)					•		•		•			175
硅橡胶的 TGA TGA of silicone elastomers					•				•			178
BR 和 NBR 的 TGA-FTIR 联用鉴定 Identification of BR and NBR using a TGA-FTIR combination					•	•	•		•			180
CIIR 弹性体的 DSC 测量 DSC measurements of CIIR elastomers	•						•	•				182
两种氟橡胶的 DSC 比较 Comparison of two fluoroelastomers by DSC	•							•				184
SBR 中低组分的转变 Transitions of low molecular weight components in SBR	•	•	•			•		•				186
SBR 的步进扫描调制 DSC 测量 IsoStep measurements of SBR	•	•	•			•	•	•				188
与其它聚合物混合的 BR 共混物的 TGA TGA of blends of NR with other polymers					•				•			191
含 SBR 组分弹性体的 TGA TGA of elastomers containing SBR as one constituent					•				•			195
CR/NBR 共混物的 TGA 分析 Analysis of a CR/NBR blend by TGA					•				•			199
BR/NR 弹性体的 TGA-FTIR 分析 Analysis of a BR/NR elastomer by TGA-FTIR					•	•			•			203
相容聚合物共混物的玻璃化转变 Glass transition of compatible polymer blends	•							•				205
不相容聚合物共混物的玻璃化转变 Glass transition of incompatible polymer blends	•				•			•				207
弹性体玻璃化转变的 ADSC 测量 ADSC measurements of the glass transition of elastomers	•					•		•				209
弹性体的 DSC 测量 DSC measurements of elastomers	•	•			•		•	•				211

续表

标题 Title	主题 Topics							方法 Methods				页码 Page
	玻璃化转变 Glass transition	结晶度/结晶 Crystallinity/crystallization	熔融 Melting	硫化 V vulcanization	组分 Composition	计算方法/实验 Evaluation/experimental Calculation/experiment	其他 Others	DSC/ADSC/IsoStep	TGA/TGA-EGA	TMA/DLTMA	DMA	
EPDM/SBR 共混物的 TGA 和 DSC 联合分析 Combined TGA and DSC analysis of an EPDM/SBR blend	•				•	•	•	•	•			213
未填充 SBR/NR 弹性体与温度关系的 DMA 测量 Temperature-dependent DMA measurements of an unfilled SBR/NR elastomer	•										•	218
未填充弹性体共混物的力学谱 Mechanical spectra of an unfilled elastomer blend	•						•				•	219
填充弹性体共混物与温度关系的 DMA 测量 Temperature-dependent DMA measurements of filled elastomer blends	•						•				•	221
填充弹性体共混物与频率关系的测量和主曲线绘制 Frequency-dependent measurements of a filled elastomer blend and master curve construction	•						•				•	223
升温速率对油含量测定的影响 The influence of the heating rate on oil content determination					•	•			•			226
含油和不含油 SBR 的降压(真空)TGA TGA of SBR with and without oil at reduced pressure (vacuum)					•	•			•			228
压力对 NR/SBR 共混物 TGA 的影响 Influence of pressure on the TGA of an NR/SBR blend					•		•		•			230
SBR 增塑的 DSC 测量 DSC measurements of the plasticization of SBR	•							•				232
三水合铝和氢氧化镁的 TGA TGA of aluminum trihydrate and magnesium hydroxide							•		•			233
EVA 中阻燃剂的 TGA TGA of flame retardants in EVA					•		•		•			235
阻燃物质的 DSC 测量 DSC measurements of flame-retarding substances							•	•				236
矿物油的 DSC 测量 DSC measurements of a mineral oil	•	•	•			•	•	•				237
软化测定的针入 TMA 测量 Determination of softening by penetration measurements by TMA	•						•			•		239
恢复行为的测量 Measurement of recovery behavior							•			•		241
溶胀行为的测量 Measurement of swelling behavior						•	•			•		242
密封圈适用温度的测定 Determination of the usable temperature range of sealing rings	•		•				•	•				244
氧化稳定性的等温 DSC 测量 Isothermal DSC measurements of oxidation stability						•	•	•				246



目 录

应用一览表 Applications List	IV
1.热分析概论 Introduction To Thermal Analysis	1
1.1 差示扫描量热法 Differential Scanning Calorimetry (DSC)	1
1.1.1 常规 DSC Conventional DSC	1
1.1.2 温度调制 DSC Temperature-modulated DSC	2
1.2 热重分析 Thermo Gravimetric Analysis (TGA)	4
1.3 热机械分析 Thermo Mechanical Analysis (TMA)	6
1.4 动态热机械分析 Dynamic Mechanical Analysis (DMA)	7
1.5 与 TGA 的同步测量 SimuLTaneous Measurements with Tga	9
1.5.1 同步 DSC 和差热分析 Simultaneous DSC and differential thermal analysis (DTA, SDTA)	9
1.5.2 逸出气体分析 Evolved gas analysis (EGA)	11
1.5.2.1 TGA-MS	11
1.5.2.2 TGA-FTIR	12
2.弹性体的结构、性能和应用 Structure, Properties and Applications of Elastomers	14
2.1 聚合物的结构 Structure of Polymers	15
2.1.1 大分子中单体的排列 Arrangement of monomers in a macromolecule	15
2.1.2 大分子的结构 Structure of macromolecules	16
2.2 聚合物的物理结构 Physical Structure of Polymers	18
2.3 聚合物材料的分类 Classification of Polymeric Materials	20
2.4 弹性体产品 Elastomeric Products	22
2.4.1 聚合物的交联 Cross-linking of polymers	22
2.4.2 弹性体的生产 Manufacture of elastomers	23
2.4.3 弹性体的组成 Composition of elastomers	23
2.5 弹性体的分类 Classification of Elastomers	24
2.6 弹性体实例 Examples of Elastomers	25
2.7 弹性体分析 Analysis of Elastomers	28
2.7.1 热效应 Thermal effects	28
2.7.2 应用概述 Application overview	29
2.7.3 弹性体分析标准方法汇总 Summary of standard methods for elastomer analysis45	30
3.弹性体的基本热效应 Basic Thermal Effects of Elastomers	33
3.1 DSC 测试效应 Measurement Effects with DSC	33
3.1.1 玻璃化转变的计算方法 Evaluation of glass transitions	33
3.1.2 结晶和熔融 Crystallization and melting	42
3.1.3 硫化反应 Vulcanization reaction	50
3.1.4 借助 ADSC 用于曲线解析 The use of ADSC to aid curve interpretation93	60



3.2 效应的 TGA 测量 Measurement Effects with TGA	64
3.2.1 组分分析的基本原理 Basic principles of compositional analysis	64
3.2.2 实验条件的影响 Influence of experimental conditions	66
3.2.3 计算方法 Evaluation possibilities	68
3.3 TMA 测量 TMA Measurements	71
3.3.1 膨胀系数的测量 Measurement of the expansion coefficient	71
3.4 DMA 实验 DMA Experiments	73
3.4.1 复合力学性能 The complex mechanical properties	73
3.4.2 DMA 曲线的计算和表示 Evaluation and presentation of DMA curves	74
3.4.3 玻璃化转变和松弛 Glass transition and relaxation	82
4.热分析的应用 Applications Of Thermal Analysis	96
4.1 橡胶的分析 Analysis of Rubber	96
4.1.1 不同种类橡胶的 TGA 分析 TGA analysis of different types of rubber	96
4.1.2 玻璃化转变 Glass transition	106
4.1.3 结晶和熔融 Crystallization and melting	108
4.1.4 DSC 和 DMA 测量的比较 Comparison of DSC and DMA measurements	121
4.2 硫化 Vulcanization	123
4.2.1 硫化反应 Vulcanization reactions	123
4.2.2 SBR 硫化度对其热分析结果的影响 Influence of the degree of vulcanization on the TA results of SBR	133
4.2.3 硫化和未硫化硅橡胶的 DSC 比较 Comparison of vulcanized and unvulcanized silicone elastomers by DSC	147
4.3 碳黑的影响 The Influence of Carbon Black	153
4.3.1 碳黑的分析 Analysis of carbon black	154
4.3.2 测定碳黑对弹性体影响的 DSC 测量 DSC measurements to determine the effect of carbon black on elastomers	156
4.3.3 弹性体中碳黑的 TGA 分析 Analysis of carbon black in elastomers by TGA	158
4.3.4 含碳黑填料弹性体的 TMA 测量 TMA of elastomers with carbon black fillers	167
4.3.5 碳黑填充弹性体的 DMA 测量 Measurement of carbon black filled elastomers by DMA	169
4.4 以单一聚合物为基础的弹性体的实验 Experiments on Elastomers Based on a Single Type Of Polymer	171
4.4.1 TGA 分析 TGA Analysis	171
4.4.2 弹性体的气体分析鉴别 Identification of elastomers by means of gas analysis	180
4.4.3 DSC 测量 DSC Measurements	182
4.4.4 低分子量成分的熔融和结晶 Melting and crystallization of low molecular weight components	186
4.5 含若干个聚合物成分的弹性体 Elastomers with Several Polymer Components	191



4.5.1 TGA 测量 TGA Measurements	191
4.5.2 弹性体组分的 TGA/FTIR 鉴定 Identification of the polymer constituents by TGA-FTIR	203
4.5.3 DSC 测量 DSC measurements	205
4.5.4 复杂弹性体的分析实例 Example of a complex elastomer analysis	213
4.5.5 DMA 测量 DMA measurements	218
4.6 弹性体中油和增塑剂的分析 Analysis of Oils And Plasticizers In Elastomers	226
4.6.1 油含量的 TGA 测定 Determination of the oil content by TGA	226
4.6.2 增塑剂对玻璃化转变的影响 Influence of plasticizers on the glass transition	231
4.7 添加剂和助剂的分析 Analysis of Additives and Auxiliary Agents	233
4.7.1 阻燃剂 Flame retardants	233
4.7.2 增塑剂 Plasticizers	237
4.8 弹性体的进一步测量 Further Measurements of Elastomers	239
4.8.1 TMA 测量 TMA measurements	239
4.8.2 DSC 测量 DSC measurements	244
5.结果的总结 Summary of Results	248
参考文献 Literature	249

1 热分析概论 Introduction to Thermal Analysis

热分析是测量材料的物理和化学性能与温度关系的一类技术的名称。在所有这些方法中,样品受控于升温、降温或等温温度程序。

测量可在不同气氛中进行,通常不是使用惰性气氛(氮气、氩气、氦气)就是氧化气氛(空气、氧气)。有时,在测试过程中气体从一种气氛切换到另一种气氛。另外有些时候有选择性变化的参数是气体压力。

Thermal analysis is the name given to a group of techniques that are used to measure the physical and chemical properties of materials as a function of temperature. In all these methods, the sample is subjected to a heating, cooling or isothermal temperature program.

The measurements can be performed in different atmospheres. Usually either an inert atmosphere (nitrogen, argon, helium) or an oxidative atmosphere (air, oxygen) is used. In some cases, the gases are switched from one atmosphere to another during the measurement. Another parameter sometimes selectively varied is the gas pressure.

1.1 差示扫描量热法(DSC) Differential Scanning Calorimetry

在 DSC 中,测量相对于惰性参比物质的流入和流出样品的热流。样品和参比物包含在分开的但是相同的坩埚中。这种安排有效地补偿了热损失和坩埚的影响。

DSC 用于测量诸如物理转变(玻璃化转变、结晶、熔融和挥发性化合物的蒸发)和化学反应这样的热效应。所获得的信息表征样品的热性能和组成。此外,用 DSC 也能测量诸如热容、玻璃化转变温度、熔融温度和结晶度这样的性能。

In DSC, the heat flow to and from the sample is measured relative to an inert reference material. The sample and reference materials are contained in separate but identical crucibles. This arrangement effectively compensates for thermal losses and the influence of the crucible.

DSC is used to measure thermal events such as physical transitions (glass transition, crystallization, melting, vaporization of volatile compounds) and chemical reactions. The information obtained characterizes the sample with regard to its thermal behavior and composition. In addition, with DSC it is also possible to measure quantities such as the heat capacity, glass transition temperature, melting temperature and degree of crystallinity.

1.1.1 常规 DSC Conventional DSC

常规 DSC 采用线性温度程序,样品和参比物(或只是空坩埚)以恒定速率升温或降温,也可进行恒温测试。往往几部分程序或程序段连接在一起生成一个完整的程序。示意性 DSC 曲线如图 1.1 所示。测试开始时曲线上的变化是由于初始的“启动偏移”(1)。在该瞬变区域,状态突然从恒温模式变为线性升温模式。启动偏移后样品为测试所设定的速率升温。启动偏移的大小取决于样品的热容和所用的升温速率。

Conventional DSC employs a linear temperature program. The sample and reference material (or just an empty crucible) are either heated or cooled at a constant rate. Isothermal measurements can also be performed. Often several partial programs or segments are joined together to form a complete program. A schematic DSC curve is displayed in Figure 1.1. The change in the curve at the beginning of the measurement is due to the initial “startup deflection” (1). In this transient region, the conditions are suddenly changed from an isothermal to a linear heating mode. After the start up deflection, the sample is heated at the rate set for the measurement. The magnitude of the startup deflection depends on the heat capacity of the sample and the heating rate used. At a glass transition, the heat capacity of

在玻璃化转变区,样品的热容增加,可观察到一个吸热台阶(2)。结晶过程(3)产生放热峰,峰面积等于结晶焓。微晶的熔融产生吸热峰(4)。化学反应取决于所涉及的反应类型给出放热或吸热峰。如果样品中存在挥发性物质如溶剂,则观察到由于蒸发产生的吸热峰(5)。最后,在较高的温度分解开始(6)。实验中使用的吹扫气体的种类经常对涉及的反应有重要影响。

可在样品冷却后通过再次测试同一样品来区分转变和反应;化学反应是不可逆的,而熔化了结晶材料当冷却或二次升温时会重新结晶。

the sample increases and an endothermic step (2) is observed. A crystallization process (3) gives rise to an exothermic peak; the area of the peak corresponds to the enthalpy of crystallization. The melting of crystallites results in an endothermic peak (4). Chemical reactions give exothermic or endothermic peaks depending on the type of reaction involved. If volatile substances such as solvents are present in the sample, endothermic peaks (5) are observed due to vaporization; the sample consequently suffers a loss in mass. Further information on such peaks can be obtained by weighing the sample before and after the measurement and by using different types of crucibles. In contrast to open crucibles, the use of hermetically sealed crucibles prevents vaporization of the sample. Finally, at higher temperatures, decomposition begins (6). The type of purge gas used in the experiment often has a major influence on the reactions involved.

Transitions and reactions can be distinguished by measuring the same sample a second time after the sample has been cooled; chemical reactions are irreversible; crystalline materials however melt then crystallize again on cooling or on heating a second time.

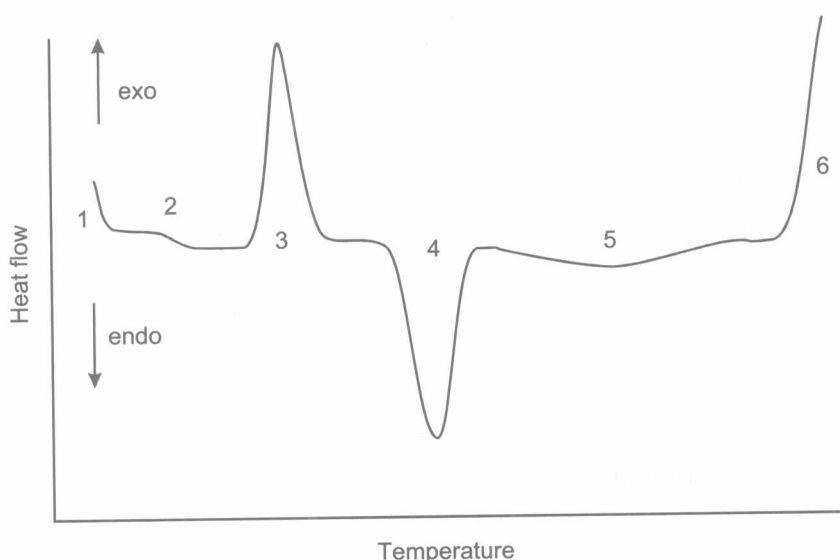


图 1.1 图示 DSC 曲线:1 初始启动偏移;2 玻璃化转变;3 结晶;4 熔融;5 汽化;6 分解
Fig. 1.1 Schematic DSC curve: 1 initial startup deflection; 2 glass transition; 3 crystallization; 4 melting; 5 vaporization; 6 decomposition.

1.1.2 温度调制 DSC Temperature-modulated DSC

调制 DSC(ADSC)是一个特别类型的温度调制 DSC。与常规 DSC 不同,温度程序用一个小周期温度变化叠加。温度程序的特征为基础升

Alternating DSC (ADSC) is a particular type of temperature modulated DSC. In contrast to conventional DSC, the temperature program is overlaid with a small periodic temperature change. The temperature program is characterized by the underlying heating rate,

温速率、温度振幅和温度周期性变化的持续时间(图 1.2)。采用准等温测试,基础升温速率也可为零。

the temperature amplitude and the duration of the periodically changing temperature (Fig. 1. 2). With quasi-isothermal measurements, the underlying heating rate can also be zero.

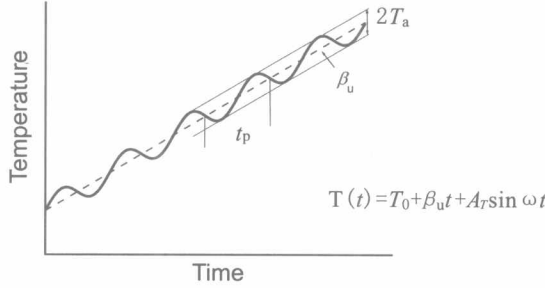


图 1.2 典型 ADSC 温度程序: β_u 为基础升温速率; T_a 为温度振幅; t_p 为周期。
Fig. 1.2 Typical ADSC temperature program: β_u is the underlying heating rate, T_a the temperature amplitude, t_p period.

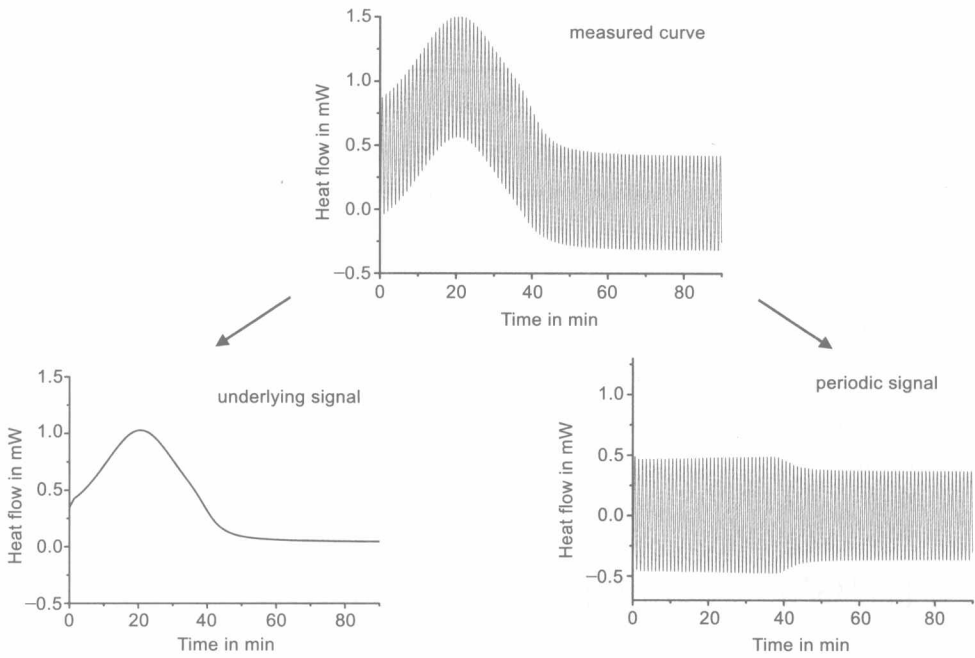


图 1.3 测得的 ADSC 曲线分离成基础和周期性信号成分。
Fig. 1.3 Separation of the measured ADSC curve into the underlying and the periodic signal components.

由于温度调制,所测得的热流是周期性变化的。该热流能分离成两部分,如图 1.3 所示。信号平均生成基本信号(总热流),它相当于常规 DSC 曲线。作为附加信息,还得到周期性信号成分。它由热流振幅和实际(调制)升温速率与热流间的相位差表征。于是从振幅和相位差测定热容(复合热容)。该技术的优势之一是能将同时发生的过程分开。

As a result of temperature modulation, the measured heat flow changes periodically. This can be separated into two parts as shown in Figure 1. 3. Signal averaging yields the underlying signal (total heat flow), which corresponds to the conventional DSC curve. As additional information, one also obtains the periodic signal component. This is characterized by the amplitude of the heat flow and the phase shift between the actual (modulated) heating rate and the heat flow. The heat capacity (complex heat capacity) can then be determined from the amplitude and the phase shift. One advantage of this technique is