

### Rheology Communications



## 中國力學學会 中國化學会 處実學专业委员会 Chinese Society Rheology

顾问: 江体乾(华东理工大学) 金日光(北京化工大学) 陈文芳(北京大学)杨挺青(华中科技大学) 韩式方(中国科学院成都分院)

**主编:** 赵晓鹏(西北工业大学)

常务主编:郑强(浙江大学)

副主编:罗迎社(中南林业科技大学) 解孝林(华中科技大学)

方 波 (华东理工大学) 张劲军 (中国石油大学.北京)

编委: 陈克复(华南理工大学) 许元泽(复旦大学) 周持兴(上海交通大学) 杨振忠(中国科学院化学研究所) 于德梅(西安交通大学) 缪协兴(中国矿业大学) 吴应湘(中国科学院力学研究所)刘跃军(湖南工业大学) 姜楠 (天津大学) 饶秋华(中南大学) 卢拥军(中国石油勘探开发研究院廊坊分院)李之达(武汉理工大学) 艾慕阳(中国石油管道科技中心) 黄丽(大庆油田勘探开发研究院) 侯万国(山东大学) 罗文波(湘潭大学) 唐国俊(华南理工大学) 孙荀英(北京大学) 唐松花(中南大学) 王国金(北京化工大学) 王启宏(武汉工业大学) 王振东(天津大学) 吴大诚(四川大学) 范椿(中国科学院力学研究所)

编辑部:杨红梅、上官勇刚(浙江大学)

编辑部地址:浙江杭州市浙大路 38 号,浙江大学高分子楼 413 邮政编码: 310027

Email: rheology\_com@yahoo.com.cn

<u>目</u>录

刊首语		1	
-----	--	---	--

贺	词		2
---	---	--	---

### 特别报道

第九届全国流变学学术年会总	结	第九届全国流变学学术年会组委会	3
流变学的诞生和研究对象	王振东		5

### 论文

电流变液与压电陶瓷复合的自耦合阻尼器 赵晓鹏 唐宏 刘 曙 1				
Studies on Structure and Properties of Muti-component Polymer Systems through Rheologica				
Methods Qiang Zheng 2				
液晶高分子溶液本构方程连续介质理论及其流动研究进展 韩式方 3				
水质对聚合物溶液拉伸流变特性的影响 李道山 5				
剪切作用下纳米粘土对聚合物熔体非线性粘弹响应的影响 杨红梅 张振威 郑强59				
延缓形成粘弹性胶束体系流变动力学性质研究 方 波 卢拥军 房鼎业等				
最小耗能原理及其在流变固体中的应用 罗迎社 唐松花 周筑宝				
SSBR/SiO2 混炼胶的动态粘弹行为 宋义虎 孙 晋 郑 强				
粘塑性金属材料高温蠕变实验及流变模型研究 罗迎社 杨柳 余敏				
Dynamic Rheological Behavior and Morphology Near Phase-Separated Region for A LCST-type				
of Binary Polymer Blends DU Miao GONG Jianhua ZHENG Qiang 104				
Mechanical and Electrical Properties of Hydrous Electrorheological Elastomers Based of				
Gelatin/Glycerin/WaterHybrid Lingxiang Gao Xiaopeng Zhao 115				
Gelling properties of waxy crude under quiescent and shearing conditions				
LI Hong-ying ZHANG Jin-jun CHEN Jun SUN Li-xin 121				

### 刊首语

各位同仁,大家好!《流变学通讯》(电子版)终于和大家见面了!

流变学在我国的研究已经有四十多年,自从 1985 年第一届流变学专业委员会成立以来, 每届委员会都把办一份流变学杂志作为重要事情之一。历经种种困难,经过各位前辈和大家 不懈的努力,我们总算前进了一大步。

流变学是研究流动和变形的科学,所涉及的学科和内容及其广泛。许多基本问题仍然处 在科学的前沿,同时它又是许多领域的技术支撑。在中国力学学会、中国化学会的领导下, 我国的流变学研究已经有了飞速发展。研究领域远远超出力学和化学的范畴,已经拓展至物 理、地质、石油、生物和许多工程技术领域。国内从事流变学及相关研究的科技人员达千人 以上,我们已经组织召开了九届专门的全国流变学学术会议和五届全国电磁流变及其应用学 术会议,主持承办了第四届亚太地区流变学学术会议。每年在国内外发表的与流变学相关的 论文数百篇。作为国际流变学会的成员,我们已经成为流变科学和技术研究的大国。

然而,与西方先进国家相比我国的流变科学和技术研究仍有很大差距。我们至今仍没有 一个专门的论坛提供国内的流变学工作者进行及时与充分的交流;我们的研究对社会发展的 推动力依然弱小,流变学工作者和社会都渴望有一个互相交流的平台。

第六届流变学专业委员会成立以来,我们着重做了两件事,一是目前设立五个专业组: 高分子流变学专业组、固体流变学与本构理论专业组、电-磁流变学专业组、石油与岩土流 变学专业组、工程应用流变学专业组,以便更好地开展学术交流活动;二是积极筹办《流变 学通讯》(电子版)。鉴于目前电子信息传媒的快速发展,经过大家的辛勤努力,我们的杂志 就要和大家见面了。希望各位同仁能精心呵护我们自己的这棵幼苗,帮助施肥、浇水,使它 能在我们大家共同的培育下茁壮成长。

祝《流变学通讯》持续发展。

#### 赵晓鹏 主编

第六届流变学专业委员会主任

2009年4月6日

### 贺 词

值此《流变学通讯》创刊之际,祝我国流变学研究人才辈出,成 果丰硕!

潮 鸦

2009年3月 杭州

热烈祝贺《流变学通讯》创刊!

"流变学通讯"一定能促进我国广大流变学工作者团结,创造国际先进水平的工作,推动我国流变学的创新研究和应用新的大发展!

### 韩式方

2009年3月9日于成都

热烈祝贺《流变学通讯》电子刊物创刊

"流变"重在创新 "通讯"贵在交流

罗迎社 谨贺 中南林业科技大学校长助理 流变力学与材料工程研究所所长 国际流变学专业委员会中国代表 2009 年 3 月 16 日子表沙

### 特别报道

### 第九届全国流变学学术年会总结

#### 第九届全国流变学学术年会组委会

金秋九月,是收获的季节。经过一年多时间精心筹备,由中国力学学会、中国化学会 流变学专业委员会主办,中南林业科技大学承办,湘潭大学、湖南工业大学和湖南省力学学 会协办的第九届全国流变学学术年会开幕式于9月29日上午在中南林业科技大学图书馆报 告厅隆重召开。出席开幕式的特邀嘉宾有中南林业科技大学副校长周先雁教授;湖南省科学 技术协会党组副书记田明星副主席;湖南省科技厅唐峰副巡视员;湖南省教育厅科技处处长 **左清**博士; 湖南省科技厅自科基金委**刘琦**主任; 中国力学学会副理事长、上海大学**戴世强**教 授; 中国化学会国际学术交流委员会副主任**张灿**高级工程师; 中国力学学会办公室**刘俊丽**副 编审;湖南省科学技术协会学会部曹争鸣副部长;湖南省力学学会理事长、国防科技大学航 天与材料工程学院系主任唐国金教授;湖南省化学化工学会秘书长庞怀林总工程师;同济大 学航空航天与力学学院院长仲政教授;原中国力学学会、中国化学会流变学专业委员会副主 任、华中科技大学工程力学系主任杨挺青教授;原中国力学学会实验力学专业委员会主任、 天津大学机械学院党委书记方一澜教授;原中国力学学会、中国化学会流变学专业委员会秘 书、中科院力学研究所苏椿研究员等。出席开幕式的还有协办单位湘潭大学十木工程与力学 学院院长、本届年会合作主席、博士导师张平教授;湖南工业大学包装与印刷学院院长、本 届年会合作主席、博士导师刘跃军教授; 承办单位中南林业科技大学研究生部部长、博士导 师、 李际平教授和科技处等相关职能处室的领导。

大会开幕式由中南林业科技大学校长助理、流变力学与材料工程研究所所长、国际流变 学会理事、本届年会组委会主席**罗迎社**教授主持;中国化学会、中国力学学会第六届流变学 专业委员会主任、西北工业大学**赵晓鹏**教授致开幕词;**周先雁**副校长代表承办学校对第九届 全国流变学学术年会的胜利召开表示热烈的祝贺,对各位领导、嘉宾和与会代表表示最诚挚 的欢迎,对这次学术盛会的隆重召开而献给中南林业科技大学五十周年校庆的这份厚礼表示 感谢,并介绍了中南林业科技大学的简况。**唐峰**副巡视员、田明星副主席、左清处长分别代 表湖南省科技厅、湖南省科学技术协会和湖南省教育厅发表了热情洋溢的讲话,对大会的召 开表示热烈的祝贺。戴世强教授、张灿副主任分别代表中国力学学会和中国化学会宣读贺信。

开幕式后,来自全国 81 所高校、科研院所和流变仪器参展单位的 190 多名代表齐聚星 城长沙神禹大酒店,围绕我国流变学基础研究和应用研究的最新进展,对当前国际流变学领 域的研究动态、前沿和发展趋势、流变学在各个领域中的应用等热点问题,以大会特邀报告、 分会场报告、技术报告和仪器参展等多种形式进行了深入的探讨与交流。会议共设八个研讨 专题,分别是:①本构模型与本构理论;②高分子溶液与熔体;③多相体系;④工业流变学; ⑤电-磁流变学;⑥岩土、地质与石油流变学;⑦食品、医药与生物流变学;⑧木材、固体 复合材料及其加工流变学。分五个分会场进行了为期 3 天的学术交流和讨论,共安排大会特 邀报告 9 个,基本涵盖了上述大部分专题,与会代表普遍反映这些报告信息量大且有一定深 度,听后很受启发。另有技术报告 3 个、分会场报告 122 个(含分会场邀请报告 23 个),是 近几年来来参会报告较多的一届年会;有五家外国仪器公司中国分公司发布了新产品信息或 进行了仪器展销。

本次会议共收到论文 219 篇,为便于会上交流,出版了中文摘要集,共收录中文摘要

169 篇。为与国际接轨并方便国际交流,不断扩大中国流变学研究在世界流变学同行研究领域的影响,为申办第17届世界流变学学术大会做前期准备,出版了英文全文论文集,该英文全文论文集收录英文论文126 篇,由中南大学出版社和 Springer 出版集团以《Journal of Central South University of Technology》特刊(SCI、EI 源刊)的形式正式出版发行。对于国内学术年会,出版英文全文论文集,尚属首次,是一次全新的尝试。

本届年会前一天的9月28日下午,在中南林业科技大学流变力学与材料工程研究所会 议室召开了中国化学会、中国力学学会第六届流变学专业委员会第二次工作会议。会前全体 委员和上级学会领导饶有兴趣地参观了中南林业科技大学"中央财政部与地方共建材料实验 中心"和流变所实验室。专业委员会会议由主任委员赵晓鹏教授主持,会议总结了本届委员 会成立近二年来的工作,讨论和部署了后二年乃至更长时期的主要工作。大家畅所欲言、讨 论热烈,对主要的工作和议题形成了共识。同时在通讯评议的基础上,评选出了首届中国流 变学杰出贡献奖3名和第五届中国流变学青年奖2名。两个上级学会的代表对委员会的工作 给予了充分肯定,均表示会一如既往地支持委员会的各项工作,并提出了一些好的建议。

在年会闭幕式上,上级学会领导为获奖者颁发了证书与奖金。下一届年会承办单位浙江 大学代表热情承诺,尽管有本届年会成功主办的压力,但浙江大学将不负众望,力争开好第 十届年会。



#### 第 九 届 全 国 流 变 学 学 术 会 议 与 会 代 表 合 影

### 流变学的诞生和研究对象

#### 王振东

#### 天津大学力学系,天津 300072

流变学是研究材料的流动和变形的科学,它是一门介于力学、化学、物理与工程科学 之间的新兴交叉学科。这里所说的材料既包括流体形态,也包括固体形态的物质。在常 温常压下,物质可分为固体、液体和气体三种状态;特殊情况下,还有等离子态和超固 态。气体和液体又合称为流体。从力学分析的角度,通常认为流体与固体的主要差别, 在于它们对于外力的抵抗能力不同。固体有能力抵抗一定大小的拉力、压力和剪切力。 当外力作用在固体上时,固体将产生一定程度的相应变形。固体静止时,可以有法向应 力和切向应力。而流体在静止时,则不能承受切向应力,微小的剪切刀将使流体产生连 续不断的变形。只有当剪切力停止作用时,流体的变形方会停止。流体这种在外力作用 下连续不断变形的宏观性质,通常称为流动性。

一般认为,英国物理学家虎克于 1678 年首先提出了,在小变形情况下,固体的变形 与所受的外力成正比。这一弹性体变形与应力关系的基本规律,后来称为虎克定律。英 国科学家牛顿在 1687 年最先提出了流体的应力和应变率成正比,后来将此称为牛顿黏 性定律,并将符合这一规律的流体称为牛顿流体,其中包括最常见的流体——水和空气, 而将不符合这一规律的流体称为非牛顿流体。上述两定律是在 17 世纪发表的,但直到 19 世纪末才由柯西、纳维、斯托克斯等人推广到三维变形和流动,并为科学界广泛接 受。从那以后,虎克弹性固体力学和牛顿流体力学随着它在许多工程分支学科中的应用, 而得到巨大的发展。但是流变学通常并不包括对上述两种情况的研究,流变学要研究更 加复杂的材料。

#### 流变学的诞生

1928年雷纳从巴勒斯坦到美国访问,并且与化学家宾汉(Bingham E C 1878~1945) 一起工作。宾汉对雷纳说,我(一个化学家)和你(一个土木工程师),一起工作解决 共同的问题,随着胶体化学的发展,这种工作方式将会变得很平常,因此需要建立一个 物理学科的分支来处理这类问题。雷纳告诉宾汉,这样的分支是存在的,并且作为连续 介质力学而被人们所认识。宾汉认为这样做不好,会吓跑化学家,需要给它起一个新的 名字。

宾汉根据古希腊哲学家赫拉克利特"一切皆流"的说法,在与一位语言学家商议之后, 提出了"流变学"(Rheology)这个名字,并于 1928 年在美国提议成立了流变学会

(Rheological Society),研究材料的变形和流动。1929年召开了流变学会的第一次会议,并创办了《流变学杂志》。这个流变学杂志,在1933年后曾停止出版;1957年作

为《Transactions of Society of Rheology》重新出版; 1978 年又恢复其最初的名字《流变 学杂志》(Journal of Rheology)。

宾汉是流变学的奠基人。他研究了悬胶、油漆、水泥等一些材料的流变特性,写了一 系列论文,特别是在1919年和H.格林联合发表的论文"油漆是一种塑性材料而不是黏 性流体",该文指出,油漆在剪切应力较小时,剪切应变率为零(或不发生流动),只有 在剪切应力超达过临界值(即屈服应力)时,才发生流动,这时应变率和应力与屈服应 力之差成正比。后来人们将具有这种流变规律或本构关系的材料或物质,称为黏塑性材 料或宾汉塑性材料(简称宾汉体)。除油漆外,石膏、悬胶、面粉团,水泥砂浆等均可 作为宾汉体来处理。圣维南的塑性流动材料和牛顿流体,均可作为宾汉体的特殊情况, 前者的流动速度为零,后者的屈服应力为零。

直到第二次世界大战爆发以前,美国流变学会仍是世界上唯一的流变学会。1939年, 荷兰皇家科学院成立了以 J.M.伯格斯为首的流变学小组。1940年,英国成立了流变学 家俱乐部。

1945年12月国际科学联合会(International Council of Scientific Unions)组织了一个流变学委员会。1947年在冯·卡门主席的主持下举行了第一次会议,代表们来自物理、化学、生物科学、大地测量、空气物理、理论和应用力学的国际联合会。委员会的职能是:对流变学的专门名词进行命名;对流变学的论文进行摘要;组织国际流变学会议等。 1968年前,国际流变学会议每5年举行一次。1968年以后,每4年举行一次。第13 届国际流变学会议是2000年8月20~25日在英国剑桥大学举行的,会议文集共刊登 578篇论文。

1973 年国际流变学委员会被接纳为国际纯粹和应用化学联合会的分支机构。1974 年 国际流变学专业委员会被接纳为国际理论和应用力学联合会的分支机构。

#### 流动的固体—流变学的研究对象之一

流动的固体,是指弹性形变与黏性流动同时存在的物体。"弹性形变"是指短暂的、能恢复原状的形变。而"黏性流动"是指持续的、不能恢复原状的形变,它也被称为"流变"。 过去一般谈固体时,是指只有弹性形变的物体;谈到流体时,是指只有黏性流动的流体。 实际上,同时具有这两种性质的物体是很多的。

用钢棒和沥青棒作如下的实验:将钢捧放在两支点上,棒的正中间放一重物,此时钢 棒弯了;当重物取走时,弯曲了的钢棒能完全恢复原状如下图 a。钢棒此时是弹性形变。 将沥青棒放到两支点上,如下图 b 那样,中间也放一重物。重物放置一段时间后取走, 沥青捧稍恢复了一点,但并没恢复原状,还是弯的。这里的沥青棒,除有弹性形变外, 己有了流变。如在沥青棒中间用手快速按一下,抬起手后,它能恢复原状,表现出很好 的弹性。但若手按下较长时间再抬起,就己不能恢复原状。同是一根沥青捧,迅速按一 下,它是弹性体;较长时间地按,又显现有流体的性质。

6

实际上很多物体,当外力作用的时间小于某一时间时,物体表现出弹性;当外力作用的时间大于这一时间,物体就会流变。这个时间就叫做物体的"缓和时间"。"缓和时间" 是一个时间阈值,当外力作用时间超过此阈值时,物体的弹性就会"缓和"而产生流变。 弹性体与流体之所以不同,也可认为只是其缓和时间不同而已。缓和时间无限长的物体, 是理想的弹性体;缓和时间等于零的物体是理想的流体。具有弹性和黏性混合性质的物体,其缓和时间既不为零,也不是无穷大,它们就是可流动的固体,或者是有弹性的流体。



钢捧与沥青捧的变形

固体表现出流动的性质,除了外力作用时间的因素外,还有温度的因素。当温度不断 升高时,大部分物体都会要流变,表现出流体的性质。

金属由应力引起的应变随时间变化的流动现象,称为蠕变。通常,升高温度或增加应力 会使蠕变加快并缩短达到断裂的时间。金属材料在恒拉应力作用下,经过一定的时间  $t_{r}$ 以后发生断裂的现象,称作蠕变断裂。在土木工程中,土地基的流变可延续数十年之久。 地下隧道竣工数十年之后,仍可出现蠕变断裂。固体材料的蠕变是流变学研究的重要课 题。

现代工业需要耐高温、耐蠕变的高质量的金属、合金、陶瓷和高强度的聚合物,因此 与固体蠕变断裂有关的流变学分支会迅速发展起来。核工业中核反应堆和粒子加速器的 发展,也为研究幅射产生的流变打开了新的领域。

在地球科学中,人们很早就知道时间过程这一重要因素。当观察地质断面时,可以看 到岩石有皱纹的褶曲结构,这是岩石在流动的证据。在几亿年的地质年代里,岩层受着 横向的力而流变成褶曲形状。在江西庐山芦林桥附近,有一处"第四纪冰川遗迹",己立 碑成为向旅游者展示岩石也在流动的景点。有人曾测量计算过冰川的黏性,大约是混凝 土的100万倍;而混凝土的黏性,大约是水的100亿倍。可见无论冰川是多么"黏",多 么难于流动,经过了几千年、几万年,终究还是在慢慢地向下流动着。流变学为研究上 地壳中有趣的地球物理现象(如冰川期以后的上升、层状岩层的与褶皱、造山作用、地 震成因以及成矿作用等)提供了物理-数学工具。对于地球内部的过程,如岩浆活动、 地幔热对流等,也可利用高温、高压岩石流变试验来模拟,从而推动了地球动力学的研 究。

#### 非牛顿流体—流变学的研究对象之二

非牛顿流体是指不满足牛顿黏性实验定律的流体,即其剪应力与剪切应变率之间不是线 性关系的流体。非牛顿流体广泛存在于生活、生产和大自然之中。

绝大多数生物流体都属于现在所定义的非牛顿流体。人身上血液、淋巴液、囊液等多 种体液,以及像细胞质那样的"半流体"都属于非牛顿流体。



自然界中整个地质年代里的蠕变, 岩石的流动尚在继续中



江西庐山第四纪冰川遗迹

近几十年以来,促使非牛顿流体研究迅速发展的主要动力之一,是聚合物工业的发展。 绝大多数聚合物,如聚乙烯、聚氯乙烯、聚丙烯酰、尼龙6、PVS、赛璐珞、涤纶、橡 胶溶液、各种工程塑料、化纤的熔体、溶液等,都是非牛顿流体。

石油、泥浆、水煤浆、陶瓷浆、纸浆、磁浆、油漆、油墨、牙膏、泡沫、液晶、泥石 流、地幔、家蚕丝再生溶液、钻井用的洗井液和完井液、感光材料的涂液、高含沙水流 等都是非牛顿流体。

在食品工业中,蛋清、炼乳、琼脂、果酱、酱油、土豆浆、番茄汁、淀粉液、苹果浆、 浓菜汤、糖稀、熔化巧克力、面团、米粉团以及鱼糜、肉糜等各种糜状食品物料,也都 是非牛顿流体。

总之,在日常生活和工业生产中常遇到的各种高分子溶液、熔体、膏体、凝胶、交联体系、悬浮体系等复杂性质的流体,差不多都是非牛顿流体。有时为了工业生产的目的, 在某种牛顿流体中,加入一些聚合物,在改进其性能的同时,也将其变成为非牛顿流体, 如为提高石油产量使用的压裂液、新型润滑剂等。

现在也有人将血液、果浆、蛋清、奶油等这些非常黏稠的流体,牙膏、石油、泥浆、油漆、各种聚合物(聚乙烯、尼龙、涤纶、橡胶等)溶液等非牛顿流体,称为软物质。

非牛顿流体有许多奇妙的特性,如射流胀大、无管虹吸、剪切变稀、拔丝、湍流减 阻等,其中有一个使人感兴趣的特性,就是部分非牛顿流体具有弹性,亦称为黏弹性流 体。当旋转杆插入黏弹性流体时,流体将沿杆向上爬,液面呈凸形。

#### 中国的流变学研究

中国最早从事流变学研究工作的可能是地质力学家。第一本翻译成中文的流变学书籍,是雷纳的《理论流变学讲义》,是由中国科学院岩体土力学研究所的6位研究人员于1965年合译出版的。

1978年制定全国力学发展规划时,认为流变学是必须重视和加强的薄弱领域。 1985年中国力学学会与中国化学会联合成立了流变学专业委员会,并在湖南长沙召

9

开了第一届全国流变学学术会议。经中国科学技术协会批准,中国流变学专业委员会对 外称为"中国流变学会",第一届的主任委员是北京大学教授、英藉华人科学家陈文芳。 第一届全国流变学会议有来自高等院校、研究和生产部门的178位代表参加,提交了 125 篇研究论文。会后由学术期刊出版社出版了《流变学进展—中国化学会、中国力学 学会第一届全国流变学会议论文集》,收入115 篇论文,按内容分别列为专题评论、非 牛顿流体力学、聚合物熔体、聚合物溶液、黏弹性和固体力学、分散体系、生物医学物 质、聚合物加工、流变测量法等9章,反映了当时中国流变学研究的状况。

1987年在成都召开了第二届全国流变学会议,并开始使用中国流变学会的会徽。1990年在上海,1993年在广州,1996年在北京,1999年在武汉,2002年在廊坊,2006年在济南,2008年在长沙,分别召开了第3至9届全国流变学会议,每届会议均正式出版了会议论文集。1995年在上海、1997年在西安、2000年在合肥召开的电-磁流变学全国会议。1991年10月在北京还召开了"中日国际流变学学术会议"。受国际理论与应用力学联合会(IUTAM)委托,1997年9月在北京召开了"带缺陷物体流变学科学研讨会"。另外,2005年在上海召开了第四届泛太平洋地区国际流变学学术会议(PRCR4)。这三次国际会议也都出版了论文集。



#### 中国流变学学会会徽

从这段流变学产生的简史可以看出,流变学从一开始就是由于工程实际的需要,从连 续介质力学和胶体化学的边缘上生长出来的新兴交叉学科,它不但从一开始就沟通了力 学和化学这两个一级学科,而且在力学中也沟通了流体力学和固体力学这两个二级学 科。

#### 流变学是沟通流体力学和固体力学的学科

反映物质或材料物理性质之间的关系式,统称为本构方程(或本构关系)。在固体力 学中,本构方程一般专指应力张量与应变张量之间的关系。在流体力学中,本构方程是 指应力张量与应变率张量之间的关系。

对于固体,人们己认识到同时体现弹性形变黏性流变的材料,是黏弹性材料。材料的 黏弹性又可分为线性和非线性两大类。若材料兼有塑性和黏性的性质,则称为黏塑性材 料,对于聚合物和一定条件下的金属往往需要考虑其黏塑性。当应力达到一定值时,黏 弹性材料呈塑性变形,或物体在弹性变形过程和塑性阶段均具有黏性效应,则称这种材料为黏弹塑性材料。许多作者己在研究工作中讨论和使用黏弹性、黏塑性和黏弹塑性的本构方程,这实际上己突破经典的固体力学本构关系,进入了固体流变学的领域。

在固体力学研究中,因要深入研究材料的破坏机理,还要类似流体力学,对固体材料 考虑应变率,研究其动力学过程。

流体力学的研究内容,在 20 世纪中期之后己有了很大的转变。在石油、化工、能源、 材料、生物工程和环保等领域所遇到的流体,己常是非牛顿流体。由于非牛顿流体涉及 许多工业生产部门的工艺、设备、效率和产品质量,也涉及人本身的生活和健康,所以 越来越受到力学工作者的重视。

流变学是力学在 20 世纪与化学、物理、工程科学交叉发展的新兴学科。中国许多力 学工作者的工作实际上己涉足流变学的研究领域,但由对流变学缺乏了解,而又未意识 到,因此也就未能从与工程科学密切联系又正蓬勃发展的流变学中吸取营养。力学发展 的关键之一,在于与各个学科及工程领域相结合,流变学正是这样一个有生命力的重要 研究领域。

(本文系作者在武汉华中科技大学召开的第六届全国流变学学术会议上的大会报告,后发表 于《力学与实践》2001年23卷4期,现略加补充,以庆祝《流变学通讯》的创刊)

### 研究论文

### 电流变液与压电陶瓷复合的自耦合阻尼器

#### 赵晓鹏\* 唐宏刘曙

#### 西北工业大学电流变技术研究所 141#, 710072, 西安

**摘要** 电流变液器件是一种智能结构,通常的电流变液装置需要外部高压电源提供对电流变液体的电激励 和计算机等系统来实施控制,因此电流变液装置都比较复杂。我们率先提出设计电流变液和压电陶瓷复合 的自耦合阻尼器,采用压电陶瓷响应外界振动而输出高电压,激励电流变液体工作,从而省去了外加高压 电源。随着外作用力的振动振幅和频率的变化,激励电流变液的压电陶瓷输出电压自动改变,阻尼器具有 自适应的特征,省去了计算机等控制系统。研制的第一代电流变液体/压电陶瓷阻尼器(弹簧直压式和楔形 施力式)实现了自适应的控制过程,显示了良好的减振性能。在第二代产品中采用了新的设计,从而能克 服第一代产品中的缺点,提高了阻尼器的结构稳定性和可靠性,使阻尼器整体性能得到提高。此外,电流 变液-压电材料复合的设计方法也可以应用到其他自适应控制系统中。

1. 引言

电流变液(Electrorheological Fluids, ER 流体)是一种智能材料,它一般是由微米(或纳米)尺度的具有高介电常数的颗粒均匀分散在绝缘的低介电常数的油相介质中形成的悬浮液<sup>[1-10]</sup>。当施加外电场时,ER 流体从流动状态转变为类固体状态,其表观粘度急增几个数量级,并达到较高的剪切应力。该过程是可逆、可控、迅速和低功耗的<sup>[1-4,10]</sup>。这些优良的机电耦合性能使 ER 流体能有效的解决机械工程中能量传递和控制等问题。

通常 ER 器件中 ER 流体工作模式可分为剪切式、流动式和挤压式<sup>[11-16]</sup>。在剪切模式中, 一个或二个电极直线或旋转运动, ER 流体受剪切作用而平行电极流动。如 Dulcos 设计的滑 片式 ER 阻尼器,它利用来自滑动电极间的 ER 剪切阻力来控制外界振动<sup>[17]</sup>。流动模式中两 电极是固定不动的,以形成一个流动通道。通过调节电场强度,ER 流动阻力可以被调控。 挤压模式的特征是:电极间隙随时间变化,中间的 ER 流体受到垂直方向上的挤压作用。研 究表明挤压模式有许多优异性能。最近,日本 Furusho 等人发展了一种 ER 触觉装置,其被 认为在虚拟现实(VR)技术中有许多可能的应用。该触觉装置的核心是一个 ER 离合驱动 器<sup>[18]</sup>。韩国 Choi 等人发展了一种剪切模式的 ER 汽车引擎座,其比传统的引擎座更能提高 乘坐的舒适性<sup>[19]</sup>。

在通常的 ER 装置中,需要外部高压电源来提供对 ER 流体的电激励。为实现精确的控制,需要计算机等控制系统来控制电压输出。因此通常的 ER 装置都比较复杂。我们提出了 ER 流体和压电陶瓷复合的自适应阻尼器,采用压电陶瓷响应外界振动而输出高电压,该高电压直接支持 ER 流体工作。这种自适应 ER 阻尼器具有更简化、更便宜、更节能的特点。本文首先介绍了我们研制的第一代 ER 流体和压电陶瓷复合的自适应阻尼器:弹簧直压式和

<sup>\*</sup>本项研究得到国家杰出青年科学基金(50025207),国家自然科学基金重点项目(59832090)和863计划 2001AA327130 资助。通讯作者, Email: <u>xpzhao@nwpu.edu.cn;</u> Tel: 029-88495950

楔形施力式。然后介绍改进后的第二代 ER 流体自耦合阻尼器。在第二代产品中采用了新的 设计,从而能克服第一代产品中的缺点,使阻尼器性能得到提高。

#### 2. 电流变液-压电陶瓷自耦合阻尼器工作原理

由于 ER 流体工作时只消耗很低的功率,可以用压电陶瓷来代替高压电源。外界振动作 用在压电陶瓷上使其产生高电压输出,将该高电压直接激励电流变液,受激的 ER 流体发生 转变,其表观粘度增加,从而导致减振系统阻尼增加,实现对外界振动的控制,此过程用图 1 表示。



图1 电流变液-压电陶瓷自耦合阻尼器工作原理图



图 2 压电陶瓷的压力-电压输出关系图

这种工作原理实现了从激励到控制的闭环控制过程。如果外界振动强,则作用在压电 陶瓷上的压力大,压电陶瓷输出的电压就高,进而对 ER 流体的激励也就增强, ER 流体的 固化作用也增强,反过来对外界振动的抑制作用也随之增大。这个过程具有自适应(自动调 节)的特征。同时用压电陶瓷代替了高压电源和计算机控制设备,使整个阻尼器的结构得以 简化。

压电陶瓷的压电输出为 *V=g<sub>33</sub>hF/S* [20],其中,*h*-压电陶瓷的高度,*S*-截面积,*g<sub>33</sub>*-压电 系数。选用山东淄博无线电陶瓷厂的 Pb(Zr-TiO<sub>3</sub>)压电陶瓷,其尺寸为 *q*7×15mm。压电陶瓷 的压力-电压输出性能见图2。当外部压力由达到70MPa时,压电陶瓷输出的电压可高达7kV。



图 3 弹簧直压式阻尼器的结构半剖图

图 4 楔形施力杆式阻尼器结构图

#### 3. 第一代 ER 流体和压电陶瓷复合的自适应阻尼器

3.1 弹簧直压式阻尼器 [21]

弹簧直压式阻尼器的活塞头和电极固定件上都打有小孔, ER 流体可以自由穿过小孔在 阻尼腔体内流动。压电陶瓷竖直固定在加压板下方。活塞和加压板之间是一个刚性的弹簧。 一组同心圆柱型电极通过电极固定件被固定在活塞杆上。阻尼器工作过程:当活塞上下振动 时,受压力激励的压电陶瓷产生高电压,这样电极间的电场就建立起来。流经电极的 ER 流 体被激励固化,系统阻尼升高,使外界振动受到抑制。

3.2 楔形施力杆式阻尼器 [22]

该阻尼器的活塞杆贯穿整个阻尼筒,在活塞杆的下方固定有一个楔形头。压电陶瓷被安放在带旋柄的小盒中。当旋柄转动时,带动偏心轴转动,使其中的压电陶瓷受挤压,输出的高压由导线接到固定在阻尼筒内部的同心圆柱电极上。当楔形头和活塞杆受外界振动上下运动时,楔形头旋紧或放松旋柄,压电陶瓷受产生高电压输出,流经电极的 ER 流体受电激励 而发生固化作用,其流动阻力增大,使活塞的振动受到抑制。制作的阻尼器外筒尺寸 Ф52×100mm。电极高度 60mm。内电极直径 40mm。内外电极间隙 1.5mm。阻尼器外筒的 壁厚 3mm。

3.3 减振实验

实验使用的 ER 流体是稀土掺杂的 TiO<sub>2</sub> 颗粒和硅油的均匀混合液体。颗粒相的体积分数为 27%,在直流电场 2.5kV/mm 时,ER 流体的屈服应力可以达到 4kPa。实验中,JZ5-5型振动激振器竖直放置,其激振杆通过加速度传感器与待测ER 阻尼器的活塞杆上端连接好。阻尼器底部固定在地面上。加速度传感器将监测到的信号送入 DHF 型电荷放大器和 CF350 信号分析仪 <sup>[23,24]</sup>。

图 5(a)和 5(b)是激振器输出功率为 75%(全功率为 100%)时测得的加速度幅值与频率的关系曲线。图 5(a)是在压电陶瓷输出未接在电极上时测得的,而图 5(b)是接上该电压输出

14

后的情况。图中Y坐标是加速度传感器测得的电信号值(单位 mV)。可以看出,加速度幅 值谱线的包络线在 5(a)中比 5(b)中的普遍稍低一些,说明当加上压电输出后,加速度幅值被 降低了。由于位移振幅  $A_d$ 和加速度幅值  $A_a$ 有如下关系  $A_d = A_a / \omega^2$ ,这说明位移振幅在加 上压电输出后也被降低了。此外,最大加速度幅值处的频率值也由未加电压时 5(a)的 57.3Hz 移动到加上电压时的 64.7Hz。说明由于压电输出的高电压的激励,ER 流体受到电激发,其 屈服应力也增大,导致阻尼器阻尼增大,阻尼器的振动受到了抑制。



图 5 激振器输出功率 75%时加速度幅值与频率的关系 (a)压电陶瓷输出未接入,(b)电压输出接入。





图 6 激振器输出功率 50%时加速度幅值与频率的关系 (a)压电陶瓷输出未接入,(b)电压输出接入。

图 6(a)和 6(b)是激振器输出功率降为 50%时测试曲线。仍可看出:图 6(b)的包络线比 6(a)中的降低一些。但是降低的程度却小了。然而,最大加速度幅值处的频率移动却仍很明显。从 未加电压时图 6(a)中的 56.6Hz 移动到加上电压时图 6(b)的 65.7Hz。这同样是由于 ER 效应, 使阻尼器内阻尼增大而使阻尼器的振动得到了抑制。图 5 和图 6 中的曲线都是尖齿状,不是 很光滑。这可能与阻尼器系统中的一些非线形因数有关。例如,楔形头与旋柄之间的摩擦。 旋柄转动力与振动位移的非线形关系及阻尼器中 ER 液体的流动等。但从一个整体性质来看, 曲线包络线的降低和最大加速度频率值的高频移动等是较明显的。

#### 4. 第二代电流变自耦合阻尼器 [25]

弹簧直压式阻尼器中压电陶瓷通过弹簧被直接安置在活塞头下面, ER 流体充满了整个 活塞腔和弹簧腔室,因此需要较多的 ER 流体,由于目前较好性能 ER 流体价格仍较高,这 会提高阻尼器成本。楔形施力杆式阻尼器中采用了类似杠杆的机械以提高作用于压电陶瓷的 压力。如果外界振动过强,可能使压电陶瓷块碎裂。第一代 ER 阻尼器中压电陶瓷的数量为 2 个,并且采用并联方式,实验发现产生的压电输出比较低,对 ER 流体的电激励也较弱, 并且楔形施力杆式阻尼器的结构稳定性也较差,这些缺陷就制约了这类自适应阻尼器的使 用。

	第一代阻尼器	第二代阻尼器
稳定性	楔形活塞易侧向滑出;	活塞以直压方式同轴运动;
	压电陶瓷并联连接	压电陶瓷呈三角对称安置
电压输出	只有2kV左右	超过5kV
工作灵敏性	楔形面与旋柄存在摩擦;	无明显摩擦面;
	载荷-ER流体-压电陶瓷激励方式	载荷-压电陶瓷-ER流体激励方式
承载能力	600N	5kN

表1两代阻尼器稳定性、灵敏性和承载能力对比

4.1 自耦合阻尼器设计与制作[26,27]

针对第一代产品中的缺点,设计制造了第二代阻尼器。图 7 是第二代自耦合阻尼器的剖视图。对比第一代自适应阻尼器,有 3 方面的改进被采用了:(1)压电陶瓷数目,安置方式和电气连接方式。在第二代阻尼器中,采用了 3 个压电陶瓷,并且呈三角形嵌入在套板中,这种三角对称嵌入式固定压电陶瓷的方法能确保阻尼器在受载荷过程中保持很好的稳定性和可靠性。压电陶瓷电气连接方式由并联变为串联,这样总的输出电压被提高了,对 ER 流体的电激励固化作用更强。(2)第二代产品中,压电陶瓷机构由位于 ER 阻尼腔下方变成了位于 ER 阻尼腔上方。这样便于外界振动载荷更有效地传递到压电陶瓷上,整个系统的工作灵敏性得到提高。(3)孔-道结构被增加到同心圆柱电极上,用以连通阻尼腔和电极间隙。由于对某些 ER 流体来说,屈服应力还不是足够的高,这种结构设计能增大 ER 流体流过孔道时的阻力,从而有效地提高系统承受外载荷的能力。表 1 列出了两代阻尼器的对比信息。改进后的新阻尼器在结构稳定性,工作灵敏性和承受载荷能力方面都有很大提高。



图 7 自耦合 ER 压电陶瓷阻尼器结构剖视图

图 8 是自耦合阻尼器实物照片。阻尼器分 5 个部分: 施力部分(包括活塞和活塞杆),压 电功率输出(包括弹簧,压簧板,压电陶瓷),阻尼部分(包括阻尼内外筒,ER 流体),电 气连接部分(导线和绝缘板),封装部分(如外筒,底座,固定螺栓等)。阻尼器工作过程: 当策动力加在活塞杆上,使活塞杆上下振动,压簧板也随活塞杆上下运动,压力通过弹簧和 绝缘板作用在压电陶瓷上,这时压电陶瓷受压输出高电压,该高电压被接到内外电极上,电 极间的 ER 流体受到电激励,其表观粘度迅速升高,在活塞运动推动下,ER 流体流过阻尼 腔下端的孔道,流过电极间隙再由阻尼腔上端的孔道回流到阻尼腔内,由于 ER 粘度剧烈增 加,阻尼力反作用在活塞上,而使活塞振动得到抑制,可以看出,该阻尼器不但能自提供能 量(不需要外界电源),而且产生的电压幅值由外界振动激励的强度来决定,外界激励强, 作用在压电陶瓷上的压力大,压电陶瓷输出的电压就高,于是能达到更优化的减振效果。这 说明该阻尼器具有自适应控制的特征。



图 8 制作的第二代 ER-压电陶瓷自耦合阻尼器实物照片。(a)外型,(b)内部零件



图 9 Ce 掺杂 TiO2 电流变液体应力-剪切率关系曲线

4.2 振动实验

实验使用 Ce 掺杂 TiO<sub>2</sub>颗粒的 ER 流体, TiO<sub>2</sub>中 Ce 掺杂量为 8.5%mol(即 Ce:Ti=8.5%), 其合成工艺已在别的文献中报道。合成工艺简述如下: 钛酸正丁脂, CeCl, 和去离子水溶 解在无水乙醇中,呈清澈黄色溶液,使用 HCl 控制 ph 值在 3-4, 后在室温下放置 12-48 小 时,形成透明凝胶。然后在 78°C 干燥 8 小时,形成固态凝胶,使该固态凝胶研碎,过筛, 然后进行分段煅烧,空气气氛,最好温度 550°C。晶态掺杂的 TiO<sup>2</sup>颗粒就制备好了。制得 的颗粒(球形,直径 5-10um, ρ=3.8g/cm<sup>3</sup>)在真空中 150°C 去水分,然后与硅油(在 25°C 时 η=50mPaS)混合制成体积分数 18%的 ER 流体,无使用任何添加剂。用 Hakke 流变仪测 量 25°C 时的流变性能。测量方式是剪切率从 0 S<sup>-1</sup>升到 300 S<sup>-1</sup>,然后降回 0 S<sup>-1</sup>。因此一次测 量会出现两条线(上升或下降段),图 9 是测量的流变曲线,测量时 ER 流体漏电流密度为 4.5uA/cm<sup>2</sup>。 ER 阻尼器的性能在 VS-300-2(东凌振动仪器公司,苏州,江苏)振动测试台上进行。 策动力由一个激振杆施加。激振杆的加速度幅值设为 3.5g,g 为重力加速度。采用扫频激励 方式,扫频速率为 8octave/min,扫频范围为 5-270Hz。激励波形是正弦,但频率随时间指数 增加,这是测试阻尼行为的常用方式。阻抗头被固定(磁性)在活塞杆上,然后激励杆压在 阻抗头上,活塞的加速度和策动力信号由阻抗头同时测得,并传给 HP-VXI 型数据分析仪。 在其他条件相同时,只是接通和断开压电输出,分别测得频率响应函数(FRF)曲线,见图 10,FRF 的输入是力(单位:N),输出是加速度(单位:m/s<sup>2</sup>),FRF 定义为: *FRF* =  $A(\omega)/H(\omega)$ ,  $A(\omega)$ 是输出, $H(\omega)$ 是输入。



分析测得的图 10 中的 FRF 曲线可以得出: (1)当接上压电输出时,FRF 曲线包络线发 生了很大变化,这说明压电陶瓷产生的高电压已经激励了阻尼腔内 ER 流体,并使 ER 阻尼 器的工作状态发生了明显变化。这点证明使用压电陶瓷来激励 ER 流体是可行的。(2)接入压 电电压后 FRF 的包络曲线普遍比未接入压电电压时的 FRF 包络线低,特别在 220-250HZ 频 率内,FRF 曲线包络下降可达 30%,这说明自耦合 ER 阻尼器对振动抑制效果是很明显的, 这点与使用外部高压电源的传统阻尼器的特征是一致的。(3)当压电电压接入后,198HZ 处 共振频率移动到了 208Hz 附近。共振峰的移动也证实 ER 流体被激励固化了。阻尼器的振动 状态也发生了明显变化。

#### 5. 结束语

尽管已设计出许多种类的基于 ER 流体的阻尼器,但将 ER 流体和压电陶瓷复合起来做 阻尼器的概念是第一次被提出来。这里提出的阻尼器使用 ER 流体作振动抑制的驱动器,压 电陶瓷作外界振动响应器和高电压输出器。激励 ER 流体固化的压电高电压同时随振动振幅 和频率的改变而变化,于是阻尼器的自动调节过程得以实现。相比于传统的 ER 阻尼器,这 类阻尼器不仅结构简单,而且具备自调控能力。第一代 ER 流体/压电陶瓷阻尼器实现了自 适应的控制过程,显示了良好的减振性能。第二代自耦合 ER 阻尼器比第一代阻尼器有很大 改进,如压电陶瓷数量、安置方式和电气连接方式不同;载荷施加机构不同;同心圆柱电极 上采用孔道结构。这些改进不仅提高了阻尼器的结构稳定性,并且也提高了工作可靠性。对 比第一代与第二代阻尼器,频响曲线上显示出更好的振幅抑制和共振模高频移动效果。

实验证明用压电陶瓷和 ER 流体复合起来形成自反馈的控制系统是可行的。此外,这种 设计方法也可以广泛应用到其他自适应控制系统中去。这种自耦合控制系统不仅可以简化设 计和制作,在实际操作中也非常方便。

#### 参考文献

- [1]. Whittle M, Bullough WA. The structure of smart fluids. Nature, 1992, 358: 373
- [2]. Halsey TC. Electrorheological fluids. Science, 1992, 258: 761-766
- [3]. Winslow WM. Induced fibration of suspension. J. Appl. Phys. 1949, 20: 1137-1140
- [4]. 赵晓鹏. 电磁流变液与智能控制. 杨大智主编智能材料与智能系统: 天津: 天津大学出版社, 2000
- [5]. X.P. Zhao, J.B. Yin, H. Tong, New advances in design and preparation of electrorheological materials and devices, in: P.L. Reece (Eds.), Smart Materials and Structures: New Research, Nova Science Publishers Inc., 2007, p. 1-66
- [6]. Zhao XP, Yin JB. Preparation and electrorheological characteristics of rare-earth-doped TiO<sub>2</sub> suspension. *Chem. Mater.* 2002, 14: 2258-2263
- [7]. Wang BX, Zhao XP. Electrorheological behavior of kaolinite-polar liquid intercalation composites. J. Mater. Chem. 2002, 12:1865-1869
- [8]. Yin JB, Zhao XP. Preparation and electrorheological activity of mesoporous rare-earth-doped TiO<sub>2</sub>. *Chem. Mater.* 2002, **14**: 4633-4640
- [9]. Wang BX, Zhao XP. Wettability of bionic nanopapilla particles and their high electrorheological activity. 2005 Adv. Funct. Mater. 2005, 15(11): 1815-18212.
- [10]. Hao T, Advanced Materials. 2001, 13:1847
- [11]. Vieira SL, Nakano M, Oke R, Nagata T. Mechanical properties of an ER fluid in tensile, compression and oscillatory squeeze test. *International Journal of Modern Physics B* 2001, 6&7: 714-722
- [12]. Wendt E,Busing KW. A new type of hydraulic actuator using electrorheological fluids. International Journal of Modern Physics B 1999, 14,15&16: 2176-2182
- [13]. Williams EW, Rigby SG, Sproston JL, Stanway R. Electrorheological fluids applied to an automotive engine mount. J. Non-Newtonian Fluid Mechanics 1993, 47: 221-238

- [14]. Choi SB, Choi YT. Sliding mode control of a shear-mode type ER engine mount. KSME international journal 1999, 13: 26-33
- [15]. Monkman GJ. The electrorheological effect under compressive stress. J. Phys. D: Appl. Phys. 1995, 3: 588-594
- [16]. Young KA, Yang B, Morishita S. Directionally controllable squeeze film damper using electrorheological fluid. *Transactions of the ASME. J. of Vibration and Acoustics* 2002, 1: 105-109
- [17]. Duclos TG. Design of device using ER fluids. SAE Transactions 1988, paper 881134
- [18]. Furusho J, Sakaguchi M. New actuators using ER fluid and their application to force display devices in virtual reality and medical treatments. *Int. J. of Modern Phys. B* 1999, **14**, **15&16**: 2151-2159
- [19]. Choi SB, Choi YT. Sliding mode control of a shear-mode type ER engine mount. KSME international journal 1999, 13: 26-33
- [20]. 李源. 压电铁电材料测量. 北京: 科学出版社, 1984
- [21]. 赵晓鹏, 唐宏, 1996 中国专利 ZL 96236145.3
- [22]. 赵晓鹏, 唐宏, 1996 中国专利 ZL 96236426.6
- [23]. 唐宏,赵晓鹏. 电流变液与压电陶瓷复合的自适应阻尼器设计和性能研究. 机械科学与 技术, 1998, 17(增): 24-26
- [24]. Tang H, Zhao XP, Liu S. Design and performance research of an adaptive damper composed of electrorheological fluids and piezoelectric ceramics. *Smart Mater. Struct.* 2003, 12: 347–354
- [25]. 赵晓鹏, 刘曙, 2002 中国专利, 申请号 02139476.8
- [26]. 刘曙, 尹剑波, 唐宏, 王允韬, 赵晓鹏. 自耦合电流变阻尼器及其性能. 机械工程学报, 2004, 40: 131-134
- [27]. Zhao XP, Liu S, Tang H, Yin JB, Luo CR. A new kind of self-coupled electrorheological damper and its vibration character. J. Intell. Mater. Syst. & Struct. 2005, 16: 57-65

部分内容发表在《力学与实践》 2006, 28(1), 7-13

#### **Studies on Structure and Properties of Muti-component**

**Polymer Systems through Rheological Methods** 

Qiang Zheng<sup>a,b\*\*</sup>

 <sup>a</sup> Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, China
 <sup>b</sup> Key laboratory of Macromolecular Synthesis and Functionalization (Zhejiang University), Ministry of Education, Hangzhou 310027, China

ABSTRACT: Rheological measurements have been a preferred approach to the characterization of the structure and properties for multi-component or multi-phase polymer systems, due to its sensitive response to changes of structure for these heterogeneous polymers. In this article, recent progress in the studies on the morphology/structure and rheological properties of heterogeneous systems is summarized mainly depending on the results by the author' group, involving the microstructure and linear/nonlinear viscoelastic behaviors of block copolymers, the correlation between the morphology and viscoelastic relaxation of LCST-type polymer blends, the relationship between the structure/properties and rheological behaviors of filled polymer blends. By means of rheological measurements, not only some new fingerprints responsible for the evolution of morphology and structure concerning these polymer systems are obtained, the corresponding results are also significant for design and preparation of novel polymer-based composites and functional materials.

**Keywords:** Heterogeneous polymers; Dynamic rheological properties; Phase- separation; Morphology and structure;

#### Introduction

The studies on rheological behavior and structure/morphology of heterogeneous polymer systems have attracted extensive attention of researchers in the polymer science and materials fields over the past decades, due to their great academic interest and increasing technological value <sup>[13]</sup>. Rheological properties of multi-component/ multi-phase polymers are related to their phase structure/morphology and the interaction of their components, and rheological response can sensitively reflect their changes. However, it is well-known that rheological behavior of heterogeneous polymers appears more complicated than that of homogeneous systems, and it is due to the complication of the correlation between the rheological behavior and structure/properties of material systems that relevant aspects have become a surge in the study on the miscibility, phase separation, structure/morphology of polymers. Furthermore, rheological

properties have been associated with some functional characteristics (*i.e.* thermal and electrical properties) of polymers in order to optimize functions/properties of ultimate materials.

In general, the rheological methods can be divided into two kinds according to the different case of force exerted<sup>[4]</sup> during tests: one is the static rheological measurements, namely the steady shear flow method under certain stress or strain, and the other, the dynamic rheological measurement, namely the oscillatory shear flow method under periodic stress or strain. For the former, the information on some interaction can be obtained by testing the flow curves of systems (*i.e.* the plots of composition  $\varphi$  versus apparent viscosity  $\eta_a$ ) or some viscoelastic parameters (*i.e.* stress difference calculated by extrusion swelling ratio). normal However, for multiphase/multi-component polymer systems, the above information is limited, and the continuous effect of stress (or strain) exerted during the static rheological testing usually leads to the change, even breakage of structure/morphology of polymer tested, especially for multiphase/multi-component polymers. Besides, it could hardly obtain accurately the information of the structure and macromolecular segment. It should be pointed out that static rheology can be integrated with optics to detect the orientation and shear stability of polymer segments and aggregates in a flow field by means of rheo-optical material functions, such as flow birefringence and flow dichroism<sup>[5]</sup>.

Compared with static rheological testing, the destruction of structure/morphology for polymers exposed to this testing process could be avoided and their linear viscoelastic response is quite sensitive to the change or formation of structure/morphology, because dynamic rheological testing is carried out under small-strain amplitude, which can be employed effectively to probe the morphology/structure of multiphase/multi-component polymer systems<sup>[4]</sup>. It has been verified that dynamic rheological testing is very effective for achieving valuable information on structure and phase behavior that can hardly be obtained by other common research measurements <sup>[2, 6-8]</sup>. In a low frequency  $\omega$  (long time) region, termed "*terminal region*" in rheology, the dynamic viscoelastic function of heterogeneous polymer systems usually deviates from the classical linear viscoelastic theory (namely the relationships among  $\omega$  and the main vicsoelastic parameters, such as dynamic storage modulus G', dynamic loss modulus G'', *i.e.*  $G^{\dagger} \propto \omega^2$ ,  $G^{\dagger} \propto \omega$  or  $G^{\dagger} \propto G^{\dagger 2}$ ) <sup>[4]</sup>. On the other hand, the so-called "*second plateau*" phenomenon appearing in terminal region is considered to be related to some heterogeneous characteristics of polymer systems, such as the polydispersity of molecular weight, the phase separation, the formation of network structure and the change of droplet shape<sup>[9-12]</sup>. Depending on the rheological properties at

terminal region, the objects of dynamic rheology has been extended to supermolecular compounds<sup>[13]</sup>. Recently, magneto-rheological suspension (MRS) in "smart fluids" has also

attracted many researchers' attention due to their industrial and academic interest<sup>[14]</sup>. People have had a partiality for applying the small strain rheometry and oscillatory shear flow because they enable people to give insights into the viscoelastic nature of the aggregates for some complex fluids before they yield, and facilitate researchers' optimizing the performance of materials.

The authors and their collaborators have focused on the applications of rheological measurements to multi-component/multi-phase polymer systems, including (1) the microstructure and linear/nonlinear viscoelasticity of block copolymers<sup>[15-17]</sup>, (2) the correlation between the morphology and viscoelastic relaxation of LCST-type polymer blends<sup>[18-23]</sup> and (3) the relationship between rheological behavior and performance of polymer composites filled with particles<sup>[24-34]</sup>. The results of the studies on the former two aspects have been reported in our previous review<sup>[2, 6]</sup>. In this article, we will mainly summarize the recent progress in the latter three aspects.

#### Microstructure and linear/nonlinear viscoelastic behaviors of block copolymers

For block copolymers, different chain segments in block copolymers may form their individual micro-phases due to the thermodynamic immiscibility, and these structures are endowed with special mechanical properties different from those of homopolymers polymerized through corresponding blocks. Hence, the correlations of their microstructure and linear/nonlinear viscoelastic behavior are important factors to determine processing and ultimate properties for these materials. Owing to the predominant properties of styrene-[ethylene-(ethylene-propylene)]-styrene block copolymer (SEEPS), the studies on the linear and nonlinear viscoelastic behavior of SEEPS were also carried out in our group <sup>[15-17]</sup>.

It is found that "second plateau" appears in low  $\omega$ s of the master curves for *G'* versus  $\omega$  through TTS (Fig. 1), which is attributed to the entanglement of macromolecular chains. This implies that hard blocks, polystyrene, act as entanglement points, resulting in a topology restraint to the movement of macro-molecular chains <sup>[15,16]</sup>. On the other hand, the nonlinear viscoelastic region can be determined through dynamic strain sweep test, and the critical shear strain \_\_\_\_\_\_ of transition from linear viscoelastic region to nonlinear viscoelastic region can be figured out, as shown in Fig. 2. These indicate that the elastic mechanism of SEEPS is destroyed by the cumulate strain <sup>[17]</sup>. When the strain is lower than  $\gamma_c$ , the simulated curve by Maxwell model (Eq. (1)) can describe the linear relaxation process of SEEPS well in the wider range than that by Ninomiya and Ferry equations (Eq. (2)). These two models are described as given as

$$G(t) = \sum_{i=1}^{n} G_i e^{-(t-t')/\lambda_i}$$
(1)

$$G(t) = [G'(\omega) - 0.4G''(\omega) + 0.014G''(10\omega)]_{\omega = 1/t}$$
(2)

in which  $G_i$  and  $\lambda_i$  are the modulus and the relaxation time of the *i*th relaxation mode, respectively. Meanwhile, it is noted that there exists a plateau in the long time region, which is due to the complex heterogeneous structure of SEEPS (Fig. 3). As is noted in Fig. 4, the nonlinear relaxation modulus obtained at relatively low shear strains follows the strain-time separation principle (STS), and when > 50%, a new characteristic relaxation process appears for the change of microstructure in SEEPS, which coincides with the results of dynamic strain sweep.



**Fig. 1** The master curves of dynamic storage modulus (*G'*) and loss modulus (*G''*) for SEEPS at the reference temperature  $T = 190^{\circ}$ C



Fig. 2 Effect of shear strain on the dynamicstorage and loss modulus, G' and G'', at 1 rad/s and 190 °C for SEEP



**Fig. 3** Linear relaxation modulus G(t) at various shear strains of SEEPS at 190°C and fits with Maxwell and Ninomiya equation



Fig. 4 The nonlinear stress relaxation behaviors for SEEPS at various large strains

# Correlation between the morphology and viscoelastic relaxation of LCST-type polymer blends

Recently, rheological research on multi-component polymer systems has been mainly focused on the immiscible systems. And for such systems, there often exists a characteristic relaxation in a long time region. However, the investigation of the system's rheological response in the homogenous regime has been seldom dealt with, especially for their phase-separation boundary region. A clear conclusion on the complicated thermo-rheological mechanism during the phase-separation of homogenous polymers has yet to be drawn. In order to study the correlation between the phase behavior and dynamic rheological characteristic of LCST-type polymer blends, poly (methyl methacrylate) and poly ( $\alpha$ -methyl styrene-co-acrylonitrile) (PMMA/ $\alpha$ -MSAN) blend is selected as model system, in which the miscibility derives from the so-called "*repulsion effect*" <sup>[35]</sup>. The influence of thermal-induced viscoelastic relaxation on their phase behavior has been examined by means of rheological measurements <sup>[8, 23]</sup>.

There exist some characteristic thermo-rheological behaviors of polymer blends near phase boundaries induced by great concentration fluctuations from homogeneous to heterogeneous region. Fig. 5 gives the  $\omega$  dependence of G', loss tangent tan $\delta$ , linear relaxation modulus G(t) and relaxation time spectrum  $H(\tau)$  for  $\alpha$ -MSAN and PMMA/ $\alpha$ -MSAN (80/20) blend. In low  $\omega$  (long time) region, the shoulder appearing in G' or G(t), the peak in tan $\delta$  and the additional relaxation in  $H(\tau)$  are all characteristic thermo-rheological response. Obviously, these rheological parameters' deviating from linear rheological model seems a useful approach to assessing the critical point of phase-separation in polymer blends.

Moreover, an initial sharp increase in complex modulus  $G^*$  in low  $\omega$  region induced by the phase-separation is attributed to the highly interconnected  $\alpha$ -MSAN-rich and PMMA-rich phases, and the subsequent decrease is the result of the loss of interconnectivity between the two phases induced by the breakup and coarsening of the phase-separated domains. On the other hand, the influence of interfacial tension (namely, the ratio of interfacial tension  $\alpha$  to the volume average radius  $\overline{R}_{\nu}$  of the dispersed phase,  $\alpha/\overline{R}_{\nu}$ ) is often assumed to be 0 or 1000 N/m<sup>2</sup> in previous literature <sup>[19, 36]</sup>, because it is difficult to measure  $\alpha$  in the melt. However, the influence of  $\alpha$  during real phase-separation is not as ideal as the assumption. Here, according to the calculated  $\alpha/\overline{R}_{\nu}$ , a satisfactory description can be given for the viscoelastic behaviors of 80/20 PMMA/ $\alpha$ -MSAN blends<sup>[37, 38]</sup>, based on the Palierne's emulsion model and Bousmina's emulsion model, as given in Eq. (3), (4) and (5).

$$G^{*}(\omega) = G_{m}^{*}(\omega) \frac{1 + 3\phi H(\omega)}{1 - 2\phi H(\omega)}$$
(3)

where

$$H(\omega) = \frac{4(\frac{\alpha}{\overline{R_{\nu}}})[2G_{m}^{*}(\omega) + 5G_{d}^{*}(\omega)] + [G_{d}^{*}(\omega) - G_{m}^{*}(\omega)][16G_{m}^{*}(\omega) + 19G_{d}^{*}(\omega)]}{40(\frac{\alpha}{\overline{R_{\nu}}})[G_{m}^{*}(\omega) + G_{d}^{*}(\omega)] + [2G_{d}^{*}(\omega) + 3G_{m}^{*}(\omega)][16G_{m}^{*}(\omega) + 19G_{d}^{*}(\omega)]}$$
(4)

$$G_{b}^{*} = G_{m}^{*} \frac{2(G_{d}^{*} + \frac{\alpha}{\overline{R}_{v}}) + 3G_{m}^{*} + 3\phi(G_{d}^{*} + \frac{\alpha}{\overline{R}_{v}} - G_{m}^{*})}{2(G_{d}^{*} + \frac{\alpha}{\overline{R}_{v}}) + 3G_{m}^{*} - 2\phi(G_{d}^{*} + \frac{\alpha}{\overline{R}_{v}} - G_{m}^{*})}$$
(5)

27



Where  $G_m^*(\omega)$ ,  $G_d^*(\omega)$ , and  $G_b^*(\omega)$  are the complex shear moduli of the matrix, the dispersed phase, and the blend, respectively;  $\phi$  is the volume fraction of the dispersed phase.

**Fig. 5** Frequency  $\omega$  dependence of storage modulus G', loss tangent tan $\delta$ , linear relaxation modulus G(t) and relaxation time spectrum  $H(\tau)$  for (a, b, c, d)  $\alpha$ -MSAN and (a', b', c', d') (80/20) PMMA/ $\alpha$ -MSAN blends under different temperatures<sup>[23]</sup>.

Fig. 6 depicts the evaluations of the rheological behaviors by using two kinds of emulsion models for the phase-separated 60/40 PMMA/ $\alpha$ -MSAN blends and 80/20 PMMA/ $\alpha$ -MSAN blends at 180 °C. It is worth noting that these two emulsion models could be hardly valid for 60/40 PMMA/ $\alpha$ -MSAN blend because the blend with this composition shows co-continuous morphology even after being annealed for a long time and this morphology dissatisfies the assumption of these two emulsion models. However, it can be seen in Fig. 6(b) that for 80/20 PMMA/ $\alpha$ -MSAN blend, the predictions by two models are approximate and good agreement between theoretical and experimental curves can be achieved over the whole investigated  $\omega$ s for the blends. It is suggested that Palierne's emulsion model and Bousmina's emulsion model are effective for the prediction of the variation of phase behavior and viscoelastic behavior of polymer blends with insular morphology.



Fig. 6 Evaluations of the rheological behaviors at 180 °C with two kinds of emulsion models for the phase-separated (a) 60/40 PMMA/α-MSAN blends and (b) 80/20 PMMA/α-MSAN blends <sup>[23]</sup>.

#### Structure/Properties and Rheological Behavior for Filled Polymer blends

The incorporation of the filler into the filled polymer blends will result in the variation of their flow behavior and then their processing capabilities. Therefore, the investigation of/into/about the melt rheology for filled polymer systems has attracted extensive attention. The authors and their collaborators have carried out some systemic research on the correlation between the structure/property and rheological response for different kinds of filled polymer systems. Here, the results for styrene butadiene rubber (SSBR)/ SiO<sub>2</sub> <sup>[34]</sup> and hydroxyl-terminated polydimethylsiloxane (PDMS)/carbonate calcium (CaCO<sub>3</sub>)<sup>[33]</sup> are mainly introduced.

The mechanisms of Payne effect for reinforcement and nonlinearity still remain controversial <sup>[39]</sup>. The dependence of visoelastic functions on  $\omega$  and  $\gamma$  for solution- polymerized SSBR filled with SiO<sub>2</sub> has been investigated for the purpose of probing mechanism of Payne effect <sup>[33]</sup>. It was found that the nonlinear viscoelastic behavior of the filled rubber is similar to that of unfilled SSBR, which is inconsistent with the general concept that this characteristic comes from the breakdown and reformation of the filler network. Fig. 7 presents  $\gamma$  dependence of *G'* and tan $\delta$  for SSBR filled with different loadings of SiO<sub>2</sub> and their corresponding master curves. It is interesting that the curves plotting either *G'* or tan $\delta$ , versus  $\gamma$  for the filled rubber, can superpose on that for the unfilled one, suggesting that the primary mechanism for the Payne effect is mainly dealt with the nature of the entanglement network in rubbery matrix. It was found that the filler network influences the characteristic strain for the onset of molecular disentanglement as well as *G'* and tan $\delta$  values due to the filler-rubber interaction, and it is believed that the existence of a synergism between the breakdown and reformation of the filler network and the molecular



**Fig.7** The strain  $\gamma$  dependence of (a) storage modulus *G*' and (b) loss tangent tan $\delta$  for SSBR filled with different loadings of SiO<sub>2</sub> at 150°C and (a', b') their corresponding master curves <sup>[34]</sup>.

disentanglement result in the enhancement of the Payne effect and improvement of the mechanical hysteresis at high strain amplitudes. Moreover, the vertical and the horizontal shift factors for constructing the master curves could be well understood on the basis of the reinforcement factor  $(f(\varphi) = G'_0(\varphi)/G'_0(\varphi=0))$ , where  $G'_0$  is the modulus at low  $\gamma$ ) and the strain amplification factor  $(A(\varphi) = \gamma(\varphi)/\gamma(\varphi=0))$ , respectively. Meanwhile, according to the modified Guth-Gold function,  $f(\varphi)$  and  $A(\varphi)$  reflecting the reinforcement effect of the fillers can be also obtained<sup>[40, 41]</sup>.

$$f(\varphi) = 1 + 2.5k_1\varphi + 14.1^*(k_1\varphi)^2 \tag{6}$$

$$A(\varphi) = 1 + 2.5k_2\varphi + 14.1^*(k_2\varphi)^2 \tag{7}$$

where  $k_1$  is an adjustable parameter responsible for an effective filler volume fraction due to the existence of bound rubber and  $k_2$  takes an effective  $\gamma$  of the rubbery phase under the existence of filler network into account. Fig. 8 gives the influence of filler volume fraction  $\varphi$  on  $f(\varphi)$  and  $A(\varphi)$  for SSBR filled with SiO<sub>2</sub> and surface-modified SiO<sub>2</sub> the solid lines being data calculated by Eq. (6) and (7). It can be found that a decrease in  $f(\varphi)$  is ascribed to the weakening of the filler-filler interaction and improvement of the filler dispersion induced by the surface modification of SiO<sub>2</sub>. However, strain amplification could hardly be affected by the variation of the surface nature of SiO<sub>2</sub>.



**Fig. 8** The dependence of (a) concentration shift factor  $f(\varphi)$  and (b) strain amplification factor  $A(\varphi)$  on the filler volume fraction  $\varphi$  for SSBR filled with SiO<sub>2</sub> and surface-modified SiO<sub>2</sub>. The solid lines in (a) and (b) are calculated by equations (6) and (7), respectively <sup>[34]</sup>.

On the other hand, the steady data and dynamic data can be correlated effectively based on the "*Cox-Merz*" rule (as shown in Eq. (8) and (9)). Hence, the rule has been extensively employed for transforming rheological data or for checking consistency of data collected through different experimental modes, which is often applicable to most concentrated polymer systems, including the melts, concentrated solutions and semidilute solutions, as well as some particle filled systems  $^{[42, 43]}$ . Accordingly, the rule can be used to predict  $\eta(\dot{\gamma})$  of the materials in the case that their  $\eta(\dot{\gamma})$ is difficult to measure. Furthermore, the rule can also be used to investigate the microstructure of materials  $^{[40]}$ .

$$\eta\left(\dot{\gamma}\right) = \left|\eta^{*}\left(\omega\right)\right|_{\omega=\dot{\gamma}} \tag{8}$$

$$\tau(\dot{\gamma}) = \left| G^*(\omega) \right|_{\omega = \dot{\gamma}} \tag{9}$$

Based on the aforementioned "Cox-Merz" and modified "Cox-Merz" rule, the steady and dynamic rheological properties of PDMS filled with different volume fractions of CaCO<sub>3</sub> have been investigated. Fig. 9 presents the comparison of the steady rheological response and the dynamic rheological response for PDMS filled with different volume fractions of CaCO<sub>3</sub>. It is obvious that there exists a critical  $\Phi$  ( $\Phi_c = 3.6\%$ ) for the suspensions, referred to as "*percolation threshold*", below which the "Cox-Merz" rule is competent over the whole shear regions; whereas beyond  $\Phi_c$ the rule breakdowns in the whole shear regions, and steady shear functions are lower than data collected from dynamic tests. The reasons for this phenomenon are believed to be the formation of percolated filler network structure and contributions of nonhydrodynamic forces and the deviation in high  $\dot{\gamma}$  s may be related to the unstable flow and interfacial slippage. Moreover, using a concentration-dependent parameter  $B(\Phi)$ , master curves of dynamic complex modulus  $|G^*|$  as a function of  $\omega$ , and shear stress  $\tau$  as a function of  $\dot{\gamma}$  for all PDMS/CaCO<sub>3</sub> suspensions, could be obtained through shifting  $|G^*|$  curves along the ordinate, and  $\tau$  functions along the abscissa using different  $B(\Phi)$  as shifting factor. Figure 10 presents master curve of  $\tau$  versus  $|G^*|$  and steady viscosity  $\eta(\dot{\gamma})$  versus complex viscosity  $|\eta^*(\omega)|$  for PDMS/CaCO<sub>3</sub> suspensions with different filler volume fractions  $\Phi$ . It should be pointed out that the reasonable superposition range is restricted only in the high  $\omega$  or  $\dot{\gamma}$  regions.



Fig. 9 Comparison of the steady and dynamic rheological properties for PDMS/CaCO<sub>3</sub> suspensions with different filler volume fractions  $\Phi$ : (a) Comparison between the shear rate  $\dot{\gamma}$  dependence of the steady state  $\eta(\dot{\gamma})$  (open) and the frequency  $\omega$  dependence of complex viscosity  $|\eta^*(\omega)|$  (filled)<sup>[33]</sup>.



Fig. 10 (a) Master curve of shear stress  $\tau$  and complex modulus  $|G^*|$  and (b) master curve of steady viscosity  $\eta(\dot{\gamma})$  and complex viscosity  $|\eta^*(\omega)|$  for PDMS/CaCO<sub>3</sub> suspensions with different filler volume fractions  $\Phi^{[33]}$ .

#### Conclusions

The examination of correlation between the morphology/structure and rheological properties for block copolymers, LCST-type polymer blends and particle-filled polymer systems has been believed to be valuable and significant to probing and studying the microstructure evolution of heterogeneous systems.

The linear/nonlinear characteristic relaxation behavior of block copolymers in long time region is the sign for the transition of their microstructure. In low frequency  $\omega$  (long time) region,
the appearance of the shoulder in dynamic storage modulus G' or linear relaxation modulus G(t), the peak in loss tangent  $tan\delta$  or the additional relaxation in relaxation time spectrum  $H(\tau)$  can be employed as effective criteria to assess the critical point of phase-separation in polymer blends. Furthermore, based on the studies on the rheological behavior for styrene butadiene rubber/silica (SSBR/SiO<sub>2</sub>) composites, their Payne effect, *i.e.* strain-dependent dynamic modulus effect, is attributed to the entanglement network of rubber matrix. For hydroxyl-terminated polydimethylsiloxane/carbonate calcium (PDMS/CaCO<sub>3</sub>) composites, when  $\Phi$  is lower than percolation threshold  $\Phi_c$ , the "Cox-Merz" and modified "Cox-Merz" rule is applicable to the transformation of steady and dynamic rheological data.

#### Acknowledgement

This work was supported by the National Basic Research Program of China (No. 2005CB623800) and The Key Program of the National Natural Science Foundation of China (No. 50633030).

#### References

- 1 Ferry, J D. "Viscoelastic Properties of Polymers", Wiley, New York, 1980, p. 56.
- 2 Han, J H and Feng, C C. Polymer, 1995, 36 (12): 2451-2462.
- 3 Zheng Q, Zuo M. Chin J Polym Sci, 2005, 4: 341-354.
- 4 Utracki L A. Polymer Alloys and Blends. New York: Carl Hanser, 1989.
- 5 Gason S J, Smith T A, Boger D V, Dunstan D E. Polymer, 2001, 42: 7755-7764.
- 6 Du M, Zheng Q, Yang H M. J Soc Rheo Japan, 2003, 31: 305-311.
- 7 Zheng Q, Zuo M. Frontiers of Mater Sci Chin, 2007, 1: 1-6.
- 8 Zuo M, Zheng Q. Wang W J. Chin J Polym Sci, 2007, 25: 1-8.
- 9 Onogi S, Matsumoto T. Polym Eng Rev, 1981, 1: 45-87.
- 10 Graebling D, Benkira A, Gallot Y, Muller R. Eur Polym J, 1994, 30: 301-308.
- 11 Svoboda P, Ougizawa T, Inoue T, Kressler J, Ozutsumi K. Macromolecules, 1997, 30: 1973-1979
- 12 Floudas G, Pakula T, Fischer E W. Acta Polym, 1994, 45: 176-181.
- 13 Fahrlander M, Fuchs K, Mulhaupt R, Friedrich C. Macromolecules, 2003, 36: 3749-3757.
- 14 Klingenberg D J. AIChE J, 2001, 47: 246- 249.
- 15 Zheng Q, Wang W J, Yu Q M, Yu J, He L, Tan H. J Polym Sci Part B: Polym Phys, 2006, 44: 1309-1319.

- 16 Wang W J, Zheng Q, Yu Q M. Chin Sc. Bull, 2005, 50: 2171-2175.
- 17 Wang W J, Zheng Q. J Mater Sci, 2005, 40: 5545-5547.
- 18 Zheng Q, Du M, Yang B B, Wu G. Polymer, 2001, 42: 5743-5747.
- 19 Du M, Gong J H, Zheng Q. Polymer, 2004, 45: 6735-6740.
- 20 Zheng Q, Peng M, Song Y H, Zhao T J. Macromolecules, 2001, 34: 8483-8489.
- 21 Zuo M, Peng M, Zheng Q. Polymer, 2005, 46: 11085-11092.
- 22 Zuo M, Peng M, Zheng Q. J Polym Sci Part B: Polym Phys, 2006, 44: 1547-1555.
- 23 Zuo M, Zheng Q. Macromol Chem Phys, 2006, 207: 1927-1937.
- 24 Zheng Q, Zhang X W, Pan Y, Yi X S. J Appl Polym Sci, 2002, 86: 3166-3172.
- 25 Zhang X W, Pan Y, Zheng Q, Yi X S. J Appl Polym Sci, 2002, 86: 3173-3179.
- 26 Zheng Q, Cao Y X, Du M. J Matt Sci Lett, 2004, 39: 1813-1814.
- 27 Hu H G, Zheng Q, Tao X L. Chem J Chin Univ, 2004, 25: 985-987.
- 28 Hu H G, Lin J, Zheng Q, Xu X M. J Appl Polym Sci, 2006, 99: 3477-3482.
- 29 Cao Y X, Du M, Zheng Q. Chin Chem Lett, 2004, 15: 567-570.
- 30 Dong Q Q, Zheng Q, Du M, Song Y H. J Soc Rheo Japan, 2004, 32: 271-276.
- 31 Yang H M, Zheng Q. Chin Chem Lett, 2004, 15: 74-76.
- 32 Yang H M, Zheng Q. J Matt Sci Lett, 2003, 22: 1431-1433.
- 33 Xu X M, Tao X L, Zheng Q. J Appl Polym Sci, 2008, 107: 1590-1597.
- 34 Sun J, Song Y H, Zheng Q, Tan H, Yu J, Hong L. J Polym Sci Part B: Polym Phys, 2007, 45: 2594-2602.
- 35 Kambour R P, Bendler J T. Bopp R C. Macromolecules, 1983, 16: 753-757.
- 36 Kapnistos M, Hinrichs A, Vlassopoulos D, Anastasiadis S H, Stammer A, Wolf B A. Macromolecules, 1996, 29: 7155~7163.
- 37 Palierne J F. Rheol Acta, 1990, 29: 204-214.
- 38 Bousmina M. Rheol Acta, 1999, 38: 73-83.
- 39 Payne A R. J Appl Polym Sci, 1962, 6: 57~63.
- 40 Guth E, Gold O. Phys Rev 1938, 53: 322.
- 41 Trabelsi S, Albouy P A, Rault J. Macromolecules, 2003, 36:9093~9099.
- 42 Gleissle W, Hochstein B. J Rheol, 2003, 47: 897~910.
- 43 Berg R F. J Rheol, 2004, 48(6): 1365~1373.

# 液晶高分子溶液本构方程连续介质理论及其流动研究进展1

#### 韩式方

#### 中国科学院成都计算机应用研究所,成都,610041,中国

Abstract: Present review is given to report advances in research on continuum theory of constitutive equation of liquid crystalline (LC) polymer liquids, Influence on of un-symmetric stress tensor on material functions, vibrational shear flow of the fluid with small amplitudes, rheology of anisotropic suspension. A new concept of simple anisotropic fluid is introduced. On the basis of principle of anisotropic simple fluid stress behaviour is described by velocity gradient tensor F and spin tensor W instead of velocity gradient tensor D in the classic Leslie-Ericksen continuum theory. Two relaxation times are introduced:. Analyzing rheological nature of the fluid and using tensor analysis a general form of the constitutive equation of co-rotational type is founded. More general model LCP-H is developed for the fluid. The un-symmetry of the shear stress are predicted by the present continuum theory for anisotropic viscoelastic fluid - LC polymer liquids. The influence of the relaxation times on material functions is specially studied. It is important to study the unsteady vibrational rotating flow with small amplitudes, as it is a best way to obtain knowledge of elasticity of the LC polymer i.e. dynamic viscoelasticity. For the shear-unsymmetric stresses, two shear stresses are obtained thus two complex viscosities and two complex shear modulus (i.e. first and second one) are introduced by the constitutive equation which are defined by rotating shear rate introduced by author. For the fluid two stability problems such as stability of hydrodynamic flow and orientational motion are discussed. The polymer suspension systems exhibit anisotropic character.. The experiments show that the PNC systems can exhibit significant shear-thinning effects. The research shows that for more concentrated polymer nano-suspensions the first normal stress difference change from positive to negative, which is similar to LC polymer behavior.

**Key words:** non-symmetric constitutive equation, anisotropic fluid, liquid crystalline polymer, material function,, stability, hydrodynamic flow, orientational motion, vibrational shear flow with small amplitude, rheology of polymer suspension

1 引言

液晶(LC)高分子是上世纪末迅速发展起来的一类新型高性能高分子材料,它的独特的优异性能引起世界各国的高度重视。已成为高新技术的新材料,特别是液晶复合材料和纳米复合材料,有广阔的应用前景。液晶高分子是一类各向异性非牛顿流体(材料),它的流变特性显著区别

sfh5578@yahoo.com.cn

基金项目: 国家自然科学基金资助项目(No. 10772177)

<sup>&</sup>quot;作者简介:韩式方,中国科学院成都计算机应用研究所研究员,德国洪堡基金会研究学者,

于一般的各向同性材料或流体(周其凤,1994;江体乾,2004;韩式方,2000,2008)。因此,国际流变 学界对液晶高分子流变学的研究长期以来极为重视,并取得了一系列研究成果。我国很重视液 晶高分子理论研究及其应用,1987年在上海召开首次高分子液晶态学术会议。自1989年至2000 年先后召开了七次高分子液晶态学术会议。自2002年至今又分别召开了第八、九、十次高分 子液晶态与超分子有序态学术会议,其中包括流变学研究论文。由此看出对高分子液晶态研究 的重视。 然而,我国在液晶高分子流变学研究方面起步甚晚,有待进一步发展。

在液晶高分子溶液和熔体理论中有从分子理论和连续介质理论等两方向的研究结果,一些 有关高分子材料的书中大多侧重从分子理论出发,较少涉及连续介质理论.液晶高分子溶液和 熔体可以看成是具有特殊物理化学性质的连续介质,目前,在连续介质理论方面有 Leslie-Ericksen 的连续介质理论和 Volkov 和 Kulichikhin 理论,Leslie-Ericksen 理论是理性连续 介质力学原理与低分子液晶理论结合,其结果已被广为应用于液晶和液晶高分子研究中,得到 了高分子科学的同行的一定程度认可.在专著"液晶高分子"(周其风,1994)中,特别设置了"液 晶相连续体理论"一节,这是 Leslie-Ericksen 理论在液晶理论中的应用,并论述了由连续介质 理论预测出的液晶高分子一系宏观行为.。

在工业流程及自然界存在不少各向异性材料和物质,例如液晶、生物材料、地幔构造及宇宙物质等.纤维悬浮液也是一类各向异性流体 (Altan, Gucei, Pipes, 1992),纤维在流体中的取向影响聚合物的特性.因此,研究各向异性材料的科学不仅涉及液晶科学的问题,而且还对其它领域或材料具有更广泛的理论指导意义.液晶是一类典型的各向异性液体,有广泛前景的新型功能性高分子材料。

#### 二、 取向流体本构方程

液晶高分子是典型的各向异性粘弹流体。为了描述液晶高分子的取向特性引进向矢n,它 表征在任意一点邻域内分子的优势取向。在外力(场)作用下,对于液晶高分子,既可以产生流体的 运动,也可以引起向矢(分子取向)的取向运动两类运动不是独立的,而相互影响。与微观分子理论 不同,为了描述液晶高分子的分子取向特性,引进向矢n,是在任意一点邻域内分子最大概率的 取向。

1. Leslie-Ericksen 连续介质理论 Ericksen 和 Leslie (Leslie1966a-b,

1968,1979; Ericksen1961,1960,1962,1976) 引入内取向体力和向矢(分子取向)的取向运动,在质量守恒、动量守恒方程,能量守恒和角动量守恒基础上 Leslie 和 Ericksen (1986)发展和建立了液晶连续介质理论,以及在此理论基础上发展的近似理论,适合于低分子液晶的取向流体运动。目前,取向流体的本构理论是建立在 Leslie-Ericksen 的理论基础上。

**2. TIF 简化模型** Baleo 等(Baleo et al ,1992) 在高粘度极限下,由 Leslie-Ericksen 理论得出简化模型。

**3.刚性棒分子理论** Doi 和 Edwards (Doi and Edwards, 1986)认为高分子分子模型是刚性轴 对称分子棒。将液晶高分子溶液模拟为均长 L 无厚度的棒状分子的悬浮液。鉴于问题的统计

37

性质,引入分布函数ψ,其定义为棒状分子处于取向区间 *u* 至 *u* + *du* 内的概率,其中 *u* 为沿分子 轴的单位矢量,其方向随取向运动而变化。考虑到上述各个作用力的贡献,导出分布函数方程。

**4. Brave 近似本构方程** Brave 等(Brave et al 1993)认为刚性哑铃分子模型与棒状分子模型 是等价的。高分子溶液模拟为刚性哑铃分子集合悬浮于粘度为常数的牛顿溶剂中,在此基础上, 导出了分布函数的扩散方程。

5. 粘弹性液晶高分子各向异性模型 与经典的理论方法不同,并区别于分子理论,Volkov 和 Kulichikhin (Volkov and Kulichikhin, 1990),引入松弛张量 $\lambda_{ij}$ 和表观粘度张量 $\eta_{ij}$ 建立非线性 的 Maxwell 模型, Volkov 和 kulichikhin (Volkov and Kulichikhin, 2000)进一步在线性的各向异性 Maxwell (1867)模型基础上提出了各向异性粘弹流体的准线性本构关系,按该作者观点, 其本构方程理论适应于可恢复的小变形情形,导至非对称应力关系式。

目前,在连续介质理论方面有 Leslie-Ericksen 的连续介质理论和 Volkov 和 Kulichikhin 理论.Leslie-Ericksen 理论是理性连续介质力学原理与液晶理论结合,其结果已被广为应用于 液晶研究中,在周其风的专著(周其风,1994)中,引用 Leslie-Ericksen 理论而设置了"液晶 相连续体理论"一节。韩式方所发展的各向异性粘弹流体一液晶高分子共转型本构方程理论, 是对以上连续介质理论的发展。

#### 三、 各向异性粘弹流体共转型本构方程

一系列宏观流变学实验研究表明,液晶高分子溶液或熔体典型的特殊流变行为主要表现在以下几个方面: a、 法向应力差的特殊变化; b、 在剪切流动中产生的向矢翻转; c、 熔体挤出时的反挤出胀大; d、 由其生产高强度、高模量丝条机制等。以上本构方程理论均未成功地解释上述宏观现象。

韩式方于自 1995 年提出了建立液晶高分子 Maxwell-Oldroyd 型本构方程 (韩式方, 1995,1996,1998,1999; Han shifang,1998,1999,2000a-c),在专著 (韩式方, 2000a)中,首先论述 了液晶高分子流变学,取向流体本构方程,以及液晶高分子粘弹流体本构方程、液晶高分子 流体 B 模型以及管内定常流动等研究成果。江体乾在专著"化工流变学"(江体乾,2004)一 书中较大篇幅引用了以上液晶高分子本构方程研究成果,并在几次全国流变学会议均对其成 果进行了积极肯定。在国家自然科学基金资助下,经过较长时间研究,液晶高分子溶液共转 导数型本构方程理论的创新研究获得了新的重要进展,成功地解释了上述宏观现象,形成独 特的理论体系(韩

式 方 ,2001a-b,2002a-b,2004,2005,2006a-c,2007,20082-b; Han shifang,2001,2004,2005a-b, 2007a-c,2008a-b), 韩式方在专著(韩式方,2008)中进一步总结了2000年至2008年, 独 立完成的各向异性粘弹流体-液晶高分子本构方程理论及其非牛顿流体力学方面的创新性 研究成果。

#### 1、各向异性粘弹流体本构方程理论原理

38

韩式方(韩式方,2008a; Han Shifang 2007a-c)发展了 Green (Green, 1964 a-b)关于各向异性 简单流体的概念,在共转坐标系中引进各向异性简单流体,即在共转坐标系引进旋转张量*W*, 以替代定义中的旋转张量*R*。

为研究液晶高分子一各向异性粘弹流体的本构理论,在新的各向异性粘弹性简单流体流体概念基础上,推广共转 Oldroyd B 流体本构方程,在建立各向异性粘弹流体本构方程连续介质理论中韩式方提出以下新的理论原理 (韩式方,2008a; Han Shifang 2007a-b, 2008a):

a、根据各向异性简单流体的新定义,应力状态是变形史的泛函,即在共转坐标系中测定的全变形梯度史 F 和全自旋张量 W 变形史的泛函。b、本构方程包含取向运动和流体动力学等两类运动的贡献,以描述液晶高分子液体的各向异性。应力张量及其共转导数是变形张量其中包括变形梯度张量 F 和自旋张量 W,及其共转导数,以及由向矢构成的张量的泛函数。c、应用上随体共转导数表示的 Oldroyd B 流体本构方程,在各向同性非牛顿流体力学中较为广泛应用。因为取向液晶高分子溶液也是一类粘弹流体,所以共转 Oldroyd B 流体的本构方程是构建各向异性粘弹流体本构方程的基础。可以通过推广共转 Oldroyd B 流体模型构建各向异性粘弹流体本构方程。

在经典的 Leslie-Ericksen 理论以及 Volkov 和 kulichikhin 理论中是采用速度梯度张量 *D* 表征材料变形历史, Volkov 和 kulichikhin (Volkov 和 kulichikhin ,2000)在线性的各向异性 Maxwell (1867)模型基础上提出了各向异性粘弹流体的准线性本构关系。在研究发展了液 晶高分子流体连续介质理论中,与以上理论不同,韩式方认为各向异性粘弹流体的变形历史 应通过变形速率张量 *F* 和旋转张量 *W* 描述。作者从理性连续介质力学出发,推广 Truesdell (1951)和 Ericksen (1960)建立本构方程的原理,在推广的共转 Oldroyd B 模型基础 上,认为本构方程中的应力分量及其共转导数以及一阶 Rivlin-Ericksen 张量共转导数是 *n<sub>i</sub>*, *N<sub>i</sub>*, *A<sub>ij</sub>*和旋转张量 *o<sub>ij</sub>* 的泛函,这是主要理论创新点。应用张量分析方法,在此理论 基础上导出了非对称应力型的液晶高分子液体-各向异性弹弹流体共转导数型本构方程,由 该本构方程得出的剪切流动应力张量是非对称的,即存在第一和第二剪切应力和第一和第二表观粘度,物质函数由 3 个增至 4 个。在以上理论原理基础上,作者导出了一类有更普遍科学意义的液晶高分子-各向异性粘弹流体共转导数型本构方程.在一般情形下,本构方程可分解为以下两部分:

法向-对称应力作用部分

$$S_{ij}^{n} + \lambda_{n} S_{kl}^{o} = \mu A_{ij}^{o} + \Psi_{ij} [A_{ij}, n_{i}, N_{i}, \beta_{j}]$$
(1)

剪切-非对称应力作用部分

$$S_{ij}^{s} + \lambda_{s} S_{ij}^{s} = \boldsymbol{\Phi}_{ij} \left[ \boldsymbol{\omega}_{ij}, \boldsymbol{n}_{i}, \boldsymbol{N}_{i}, \boldsymbol{\gamma}_{j} \right]$$
<sup>(2)</sup>

40

其中: $\lambda_n$  —表征法向-对称应力松弛, $\lambda_s$ ; $\lambda_s$  —表征剪切-非对称应力松弛。其中由一般理论建立了一类新的液晶高分子本构方程 LCP-Qs 模型

$${}^{o}_{S_{ij}} + \lambda^{*}(II_{A})S_{ij} = \eta^{*}(II_{A})A_{ij} + \mu^{*}(II_{A}){}^{o}_{A_{ij}} + \beta_{1}n_{i}n_{j}n_{k}n_{s}A_{ks} + \beta_{2}n_{i}n_{k}A_{kj} + \beta_{3}n_{j}n_{k}A_{ik} + \chi_{1}n_{j}n_{s}\omega_{is} + \chi_{2}n_{i}n_{s}\omega_{js} + \chi_{3}\omega_{ij} + \chi_{4}n_{i}n_{j}n_{k}n_{s}\omega_{ks}$$
(3)

其中 
$$II_A = \sqrt{\frac{1}{2}tr(A^2)}$$

当  $\beta_2 = \beta_3, \chi_1 = \chi_2 = \chi_3 = \chi_4 = 0$  方程(1)转化为作者早期(1995-1999)提出的 液 晶高分子 Oldroyd-Maxwell 型 LCP-B 模型 . 在以上张量函数展开式系数的推导中曾应用 横观各向同性的概念,可以认为这是在三维欧氏空间是横观各向同性的。

在流变学研究中,为了研究一个新的本构方程,通常把本构方程应用于简单剪切流动, 并考察所得出的物质函数,并应用研究具体问题,以论证本构方程合理性。

# 2、 法向应力差的特殊流变学行为 ( 韩式方 ,2000,2005a,2008a;韩式方等,2002,2003,2008, Han Shifang, 200a,2007a-b,2008a ;Han Shifang et al,2005,2007)

本构方程的第一项应用是从理论预测了第一、第二法向应力差的特殊流变学行为。图 • 1 示出第一、第二法向应力差与剪切速率 γ 的曲线(随向矢角变化),图 2 显示第一、第二法向

应力差函数与剪切速率 γ 的变化关系 . 由图 1 和图 2 得出结论,向矢取向由平行流动方向 旋转(或翻转)至垂直流动方向,其法向应力差随剪切速率变化曲线的不改变走向,只改变了 曲线函数值的大小. 在图中的第一法向应力差由正值到负值,再发展为正值,图中的 第二 法向应力差 ,由负值到正值,再发展为负值,与 Baek,Larson 等(Baek,Larson 等,1993,1994; Baek 等,1993 )的实验结果比较取得较好的一致性。由 LCP-Qs 模型得出结论,当向矢取向 角由平行流动方向旋转至垂直流动方向时,向矢的旋转(或翻转)不改变法向应力差随剪切 速率变化曲线的走向,存在极大值和极小值变化趋势不变,而改变了曲线函数值的大小,即 曲线位置升高或降低. 在适当选定本构方程参数后,向矢翻转可能导至第一法向应力差曲线 完全



(a)

(b)

图 1 第一法向应力差  $\sigma_1$  (a)和第二法向应力差  $\sigma_2$  (b)与剪切速率  $\gamma$  之间关系(向矢平行和垂直流动方向) LCP – Qs 模型 1— 共转 Maxwell 模型 LCP – Qs model , 1— co-rotational Maxwell model

#### 3、 非对称应力张量 (韩式方,2008a;HanShifang,2007a,2008a)

在各向异性流体共转型本构方程连续介质理论基础上,应用 LCP-Qs 模型导出的剪切流 动的剪切应力分量是非对称的,即存在两个剪切应力,和两个表观粘度,以及存在旋转粘度, 对于轴对称剪切流动物质函数由3个增至4个.这是液晶液体作为显示介质的理论基础。在 液晶高分子液体剪切运动中存在旋转剪切应力而产生复杂的旋涡流动,当光源通过时将出现 绚丽多姿的彩色图案。

图 3 示出第一和第二表观粘度与剪切速率曲线.在各向异性粘弹流体剪切流动中存在两 个剪切应力、两个表观粘度和旋转应力,因而产生旋涡和旋转运动,这一理论机制可能成为 液晶高分子材料在现代显示技术中应用的理论基础.Volkov 和 kulichikhinm (2000)曾在线性 的各向异性 Maxwell (1867)模型基础上提出了各向异性粘弹流体的准线性本构关系,适应 于可恢复的小变形情形,导至非对称应力关系式。以上理论是建立在宏观的理性力学、连续 介质力学基础上,它适应于有限变形情形,导出非对称应力张量解析表达式,这是本理论与 V-K 理论的性区别和发展。









图 3 第一法表观粘度 $\eta_1(a)$ 和第二表观粘度 $\eta_2$  (b)与剪切速率 $\gamma$ 之间关系(随松弛时间变化) LCP-Qs

模型

a-向矢平行流动方向, b-向矢垂直流动方向

#### 4、各向异性流体小振幅振荡旋转流动 (韩式方,2008a-b; Han Shifang.2008a)

研究了各向异性粘弹流体依时性流动,即小振幅振荡剪切流动.在韩式方提出的各向异性粘弹流体 - 液晶高分子共转型本构方程理论<sup>[3-5]</sup>和物理 - 流变学机制分析基础上,并应用计算机符号运算软件 Maple,研究了小振幅振荡剪切流动,在本构方程中引进了两个松弛时间 $\lambda_n$ 和 $\lambda_s$ .对于非对称应力作用下的小振幅剪切流动,由于存在第一剪切应力和第二剪切应力分量导出了第一旋转复粘度和第二旋转复粘度.由第一和第二旋转复粘度导出的储能模量 G'<sub>n</sub>和耗能模量 G''<sub>s</sub> 与振动频率 ω之间解析表达式,与一般非牛顿流体流动情形显著不同,鉴于应力张量的非对称性引进了以下 3 个复粘度: 1、对应法向 - 对称应力作用的复合粘度  $\eta_{n}^*$ ; 2、两个对应剪切 - 非对称剪切应力作用的旋转复粘度  $\eta_{r1}^*$ 和  $\eta_{r2}^*$ .由于各向异性粘弹流体可导出两个非对称剪切应力分量,该应力分量等于法向 - 对称部分的剪切应力与剪切 - 非对称部分的剪切应力之和.

图 4 示出对应法向一对称应力作用下的小振幅振荡剪切流储能模量和耗能模量与振动 频率之间关系(随向矢角θ变化,

 $η_0 = 5.0, λ_n = 0.5, β_1 = 1.50, β_2 = 1.0, β_3 = 2.0$ ),图 5 和图 6 分别示出在剪切-非对称应力作 用下,由第一和第二旋转复粘度导出的储能模量和耗能模量与振动频率之间关系(曲线随向 矢角θ变化, λ<sub>s</sub> = 0.50, β<sub>4</sub> = 1.50, β<sub>5</sub> = 1.0).由图 1 图 3 看出,向矢翻转(director tumbling)可改变储

42

能模量和耗能模量的数值,但不改变其与振动频率之间曲线的总趋势.以上理论和结论是本 作者的创新性贡献,由本理论得出的各向异性粘弹流体 - 液晶高分子小振幅振荡剪切流动理 论预测,存在非对称应力和 3 个或更多复合粘度和复合模量,其结论与 Volkov 和 Kulichikhin (2000) 的非对称粘弹性结论是一致的.

5、各向异性流体流动稳定性(韩式方,2008a; Han Shifang, 2008c)

在研究各向异性流体运动时,不仅要考虑流体运动,还要考虑取向运动.在研究液 晶高分子熔体或溶液运动稳定性时, 既要考虑流体运动稳定性,同时要考虑取向运动稳定 性.各向异性流体流体动力学稳定性和取向运稳定性等两类稳定性研究进展.

研究各向异性非牛顿流体-液晶高分子剪切-拉伸薄板不稳定性,其速度场可以表示为

$$\mathbf{v}_1 = \mathbf{k}_1 \mathbf{x}_1 + \gamma \mathbf{x}_3, \mathbf{v}_2 = \mathbf{k}_2 \mathbf{x}_2, \mathbf{v}_3 = \mathbf{k}_3 \mathbf{x}_3$$

式中 k<sub>1</sub>,k<sub>2</sub>,k<sub>3</sub> 为 x<sub>1</sub>,x<sub>2</sub>,x<sub>3</sub>方向上的拉伸率,γ为剪切流动成分的剪切速率.这是一类 以拉伸运动为主并带有剪切成分的流动.根据韩式方发展的各向异性流体-液晶高分子共转 导数型本构方程和扰动本构方程理论,采用液晶高分子 LCP-Qs 流体模型,导出了该流体剪 切-拉伸流动扰动本构方程,并研究了该流体剪切-拉伸薄板不稳定性,其稳定性准则可表 达如下

$$\beta = k_3 - \frac{\frac{\sigma_3}{\partial \sigma_3 / \partial k_3}}{1 - \alpha(0)e^{(k_3 - k_1)t} \frac{2\gamma}{k_3 - k_1} \left(1 + \frac{2\eta}{\partial \sigma_3 / \partial k_3}\right)} \rightarrow \begin{cases} < 0 \\ = 0 \\ > 0 \end{cases}$$

由研究得出以下结论: 1、应用以上稳定性理论研究了单轴拉伸、双轴拉伸、平面拉伸和 两类椭球拉伸等 5 类典型的薄板拉伸流动,单轴拉伸是较不稳定的拉伸过程,在拉伸流动中 存在剪切运动成分使薄板拉伸流动不稳定性增加, 2、双轴拉伸流动具有抗剪切扰动的能 力,只有当剪切速率大于一临界值时,系统才会呈现不稳定状态.3、在剪切扰动作用下,平 面拉伸流动是不稳定的.在工艺实际中较难实现平面拉伸过程.因为在应用数值模拟方法研 究平面拉伸流动相对简便,所以它有一定的理论意义,在非牛顿流体力学研究中有一定数量 研究工作是关于平面拉伸流动的.4、第一类椭球拉伸流动与双轴拉伸类似,同样具有抗剪切 扰动的能力,只有当剪切速率大于一临界值时,系统才会呈现不稳定状态.5、第二类椭球拉 伸流动同样具有抗剪切扰动的能力,也只有当剪切速率大于一临界值时,系统才会呈现不稳 定状态.与双轴拉伸比较,第二类椭球拉伸显示的稳定区更大,因此,第二类椭球拉伸较双 轴拉伸更稳定.6、向矢翻转不改变以上典型拉伸流动特征







图 5 由第一旋转复粘度的储能模量  $G'_{s1}$  (a)和耗能模量  $G''_{s1}$  (b)与振动频率  $\omega$ 之间关系



图 6 由第二旋转复粘度的储能模量  $G_{s2}^{\prime}$  (a) 和耗能模量  $G_{s2}^{\prime\prime}$  (b) 与振动频率  $\omega$ 之间关系



Fig. 5 First apparent viscosity vs director angle, director is parallel to flow direction



Fig. 6 Disturbed amplitude function p(t) vs  $\lambda kt$ for orientational extensional flow with 2D disturbance (with variation of anisotropic viscosity  $\beta_5$ )

#### 6、 挤出-拉伸流动 (韩式方,2008a; Han Shifang, 2005b,2007c)

液晶高分子熔体由喷丝孔挤出流动,在紧靠近喷丝孔的流动不是一类简单的轴向拉伸流动,而是一类以拉伸为主,带剪切运动成份的流动。应用该本构方程得出纺丝拉伸流动中的无量纲轴向拉伸速度及丝条直径随拉伸方向无量纲距离的变化规律(Mantia et al, 1989; Wagner, Geiger et al,1997)丝条直径随拉伸方向距离增大而略有减小,即反挤出胀大现象。 与热致性液晶高分子的实验研究一致,表明其本构方程是合理的。共转导数基础上的模型适 合于研究液晶高分子流体力学问题。从物理机制对这一现象解释,对于各向异性粘弹流体, 旋转各向异性抵抗或平衡了弹性能量的存储,以致挤出后丝条不具备足够恢复的能量,因而, 与一般高分子熔体挤出胀大相反,观察到丝条直径略为缩小。

#### 参考文献

Altan M. C., S. I. Guceri and R.B. Pipes, 1992, Anisotropic channel flow of fiber suspensions,

#### J. Non-Newtonian Fluid Mechanics., 42(1/2): 65-83

- Baek S.-G., Magda J. J. and Larson R.G., 1993, Rheological differences among liquid-crystalline polymers I. The first and second normal stress differences of PBG solutions J. of Rheology 37 (6): 1201 – 1224
- Baek S.-G., Magda J. J. and S. Cementwala, 1993, Normal stress differences in liquid crystalline hydroxypropylcellulose solutions J. of Rheology 37 (5): 935 – 945
- Baek S.-G.,Magda J. J. ,Larson R.G. and Hudson S. D, 1994, Rheological differences among liquid- crystalline polymers II. T Disappearance of nagative  $N_1$  in densely packed

lyotropic and thermotropes

**J. of Rheology** , 38 ( 5 ): 1473 - 1503

Baleo J.N., M. Vincent and P. Navard, 1992, Finite element simulation of flow and director orientation of viscous

anisotropic fluids in complex 2D geometries, J of Rheol., 36,4,663---701

Brave A.V., R.K. Menon, R.C. Armstrong and R. A. Brown, 1993, A constitutive equation for liquid crystalline polymer solution, J. of Rheol., 37, 413---441

Doi, M. and Edwards S.F., 1986 The Theory of Polymer Dynamics, Oxford London, 1986

Ericksen J.L., 1961, Conservation laws for liquid crystals, Trans. Soc. Rheol., 5: 23 - 34

Ericksen, J.L. 1960, anisotropic fluids, Arch. Rational Mech. Anal., 4, 231-237.

Ericksen, J.L 1962, Hydrostatic thepry of liquud crystals, Arch Rational Mech. Anal. V 9 371-378

Ericksen, J.L. 1966, Phys. Fluids, 9,1205

Ericksen, J.L. 1976, Equilibrium theory of liquid crystals. Adv. Liq. Cryst. 2:233-298

Green A.E., 1964a, Anisotropic simple fluid, Proc. Roy. Soc. Londonser, A 279, p 437-445

Green A.E., 1964b, A continuum theory of anisotropic fluids, Proc. Camb. Phil. Soc.,60 p 123 – 128

Han Shifang(韩式方), 1998, Constitutive Equation of Maxwell-Oldroyd Type for Liquid Crystaline Polymer and

Its Fluid Flow, **Proc. of 3rd Int.Conference on Fluid Mechanics**, Beijing, Beijing Institute of Technology Press.

Han Shifang, 1999, Constitutive Equation of Rate type for Liquid Crystalline Polymer and Fluid Flow Bifurcation,

Proc. of 8th Asian Congress of Fluid Mech.

Han Shifang, 2001, Convective derivative approach to constitutive equation for liquid crystalline polymer

and its flow bifurcation, Prof. of 3rd Pacific Rim Conference on Rheology, Vancouver, Canada

Han Shifang(韩式方) and Wang Yubin (王毓宾), 2002 Research on Rheological Behaviour of Liquid Crystaline Polymer – Nematic Fluid, **Proc. of 6<sup>th</sup> European Conference on Rheology**, p621-622 Erlangen

Han Shifang, 2004, Constitutive equation of co-rotational derivative type for anisotropic

viscoelastic fluid Beijing: Acta Mechanica Sinica, No: 2 p 46-53, Springer

Han Shifang, 2005a, A Constitutive equation of Co-Rotational Type for Liquid Crystalline Polymer and

Anisotropic Material Functions, Keynote Lecture Advances in Rheology and its applications,

Proc. of 4<sup>th</sup> Pacific Rim Confference on Rheology ,p 22-27 Science Press USA Inc.

Han Shifang ,2005b, Computational Analytical approach to Shear-Extensional Flow in Extrusion of Anisotropic

Viscoelastic Fluid, Advances in Rheology and its applications, Proc. of PRCR 4, p 137-142 Science Press

USA Inc.

Han Shifang, Wang Yubin ,Han Yulian, 2005, Anosotropic rheological behaviour of liquid crystalline polymer,

Advances in Rheology and its applications, Proc. of PRCR 4, p 313-316 Science Press USA Inc.

Han Shifang, 2007a, An unsymmetric constitutive equation for anisotropic viscoelastic fluid

Beijing: Acta Mechanica Sinica, vol 23, No: 2, p149-158 (2007) Springer

Han Shifang, 2007b, A Constitutive Equation of Co-Rotational Type for Liquid Crystalline Polymer

and Influence of Orientation on Material Functions, J. of central South Univ. Technol. v.14 Suppl.

1, p14-18, Springer

Han Shifang, 2007c, Computational Analytical Approach to Shear -Extensional Flow in Fiber spinning of Liquid

Crystalline Polymer Melt, J. of central South Univ. of Technol., v. 14 Suppl. 1. p61-67, Springer

Han Shifang, Wang Yubin(王毓宾), Han Yulian(韩毓莲) 2007, Anisotropic Orientational Behaviour of Liquid

Crystalline Polymer, J. of central South Univ. Technol。 v. 14 Suppl. 1. p142-145 Springer Han Shifang , 2008a, Research advances in research on non-symmetric constitutive theory of anisotropic

viscoelastic liquids and its hydrodynamic Behavior, J. of central South Univ. Technol. v.

15 Suppl. 1. p1-4 Springer

Han Shifang, 2008 b, Vibrational shear flow of anisotropic viscoelastic fluid with small amplitudes, J. of central

South Univ. Technol。 v. 15 Suppl. 1. p29-32 Springer

- Han Shifang , 2008 c, Stability of shear-extensional flow in film extrusion of liquid crystalline polymer-anisotropic viscoelastic fluid , <u>AIP Conf. Proc.</u> -- July 7, 2008 -- Volume <u>1027</u>, pp. 126-128 THE XV INTERNATIONAL CONGRESS ON RHEOLOGY: The Society of Rheology 80th Annual Meeting
- Leslie F.M., 1966, Quart. J. Mech. Appl. Math., 19, 357.
- Leslie F.M., 1966, Some constitutive equations for anisotropic fluids,

Q.J. Mech. Appl. Math. 19.157-370

- Leslie F.M., 1968, Arch. Rational Mech. Anal., 28, 265.
- Leslie F.M., Theory of Flow Phenomena in Liquid Crystals ,1979, in : G.H. Brown ed. Advances in Liquid Crystals, New York : Academic , 1979, vo.1 p.1-
- Mantia F.P., and A. Valenza, 1989, Shear and nonisothermal elongational characterization of a liquid crystalline polymer, Polymer Engineering and Science, v. 29 No. 10 625 631
- Wagner M.H. A, Th.Ixner, and K. Geiger, 1997, A note on the melt strength of liquid crystalline polymer, J. Rheol. 1997, 41 (5) 1087 1093
- 韩式方,1995,非牛顿流体本构理论新进展,二,各向异性流体-液晶高分子的本构理论 .

力学研究与应用,张涵信等主编,成都科技大学出版社

韩式方, 1996, 各向异性流体-液晶高分子流变学研究 . 邀请报告,

"流变学进展",p15-21,化学工业出版社 . 第五届全国流变学会议文集,

韩式方,1998,液晶高分子 Maxwell-Oldroyd 型本构理论及流动研究 .

力学与工程应用,西南交通大学出版社.

韩式方,1999,液晶高分子本构理论及流体力学问题,"流变学进展'

第六届全国流变学会议文集, 邀请报告, 华中理工大学出版社, p17-23 王毓宾,韩式方, 1999, 溶致性液晶高分子流变行为研究,

第六届全国流变学会议文集,华中理工大学出版社,p110-111 韩式方,2000a,非牛顿流体本构方程和计算解析理论 . **专著,北京:科学出版社** 韩式方,2000b,跨越经典力学理论范畴发展流变学和非牛顿流体力学,"**力学 2000**",气象

出版社中国力学学会 "力学 2000 " 学术大会论文, p234 - p236

韩式方,2000c, 液晶高分子流体管内定常流动分岔现象研究 , "力学 2000 ", 气象出版社,

中国力学学会 "力学 2000" 学术大会论文, p257 - p259

韩式方,2001a, 液晶高分子各向异性粘弹流体本构方程研究,

#### 力学学报 , No 5 p 588-599

韩式方,2001b,流变学的前沿方向 — 液晶高分子流变学,

#### 北京: 力学与实践 No: 3, p1-6

韩 式 方,2002a 流变学在西部大开发中的作用

#### 北京:"力学与实践",vol 24, 增刊, p 5-10

韩式方,2002b,液晶高分子粘弹流体本构方程理论研究,

# **高分子液晶态与超分子有序态研究进展,周其凤主编**,p 337-341, 华中科技大学出版社

王 毓 宾, 韩 式 方, 2002 液晶高分子各向异性及其流变性质研究,

高分子液晶态与超分子有序态研究进展,周其风主编,p 342-344,华中科技大学出版社

韩 式 方,王 毓 宾,2003 液晶高分子取向特征及其流变性质研究,

#### 北京:"**力学与实践**" No 2 p12-15

王 毓 宾, 韩 式 方, 2003, 论液晶高分子取向运动 - 特殊流动及其实验证明,

流变学进展(2002), 李文阳等主编, p156 - 159,中国科技文献出版社

韩式方, 2004, 高强度液晶高分子纺丝纤维取向机制研究,

北京: **力学与实践** v 26 , p39-41 No 2

韩式方,2005,液晶高分子熔体反挤出胀大的流变学理论机制,高分子液晶态与超分子有序 态研究进展,

王玉忠 解孝林 主编, p 334-339, 四川大学出版社

韩式方,2006a,液晶高分子--各向异性流体挤出拉伸分岔研究,

#### 北京: 力学与实践 v 28 , No 3

韩式方 2006b, 液晶高分子挤出--拉伸流动的计算机智能解析理论

#### 西南交通大学学报, 增刊, 41, p22-24

韩式方,2006c,液晶高分子液体本构方程理论研究进展

邀请报告,第八届全国流变学学术会议文集,山东大学出版社,p3-21

韩式方,2007,各向异性粘弹流体-液晶高分子本构方程及其流体力学研究进展,

中国力学学会学术大会'2007论文集

韩式方, 2008 a, 各向异性非牛顿流体连续介质力学 — 液晶高分子流变学

北京:科学出版社

韩式方 2008 b, 各向异性粘弹流体小振幅振荡旋转流动,

四 川 大 学 学 报 ( 工 程 科 学 版 ) v40, p26-29, Supp 韩式方, 王毓宾, 韩毓莲, 2008 各向异性流体-液晶高分子取向特征研究,

四 川 大 学 学 报 ( 工 程 科 学 版 ) v40, Supp, p177-180 江体乾,2004,化工流变学 .华东理工大学出版社.

吴大诚、谢新光、徐建军 ,1987,高分子液晶,四川教育出版社.

周其凤,王新久著.1994,液晶高分子,科学出版社

# 水质对聚合物溶液拉伸流变特性的影响

### 李道山<sup>1,2</sup> 1. 大港油田公司采油工艺研究院, 天津 300280; 2. 天津大学化工学院, 天津 300072

**摘要:**用现代分析方法,系统分析了大港油田南部官80区块注入污水中无机离子、有机成分以及三种 细菌的含量。研究了污水中各种活性组分对聚合物溶液黏度的影响及聚合物氧化降解的机理。介绍了拉伸 流变仪的工作原理。用拉伸流变仪研究了几种典型驱油用聚合物溶液的拉伸流变特性,以及不同水质对聚 合物溶液拉伸黏度的影响。实验结果表明:在相同条件下,功能型聚合物的拉伸断裂时间长,拉伸黏度高。 配制聚合物溶液所用水的矿化度及活性组分对聚合物溶液的拉伸性能影响很大,水的矿化度及活性组分越 高,拉伸断裂时间和拉伸黏度越低。

关键词: 拉伸流变; 拉伸黏度; 污水; 聚合物驱; 功能型聚合物

当聚合物溶液通过收缩-发散的喉道时,流线收缩,流动单元在横向上变细,轴向上伸 长,从而产生拉伸流动,这是因为聚合物溶液通过孔喉时受到拉伸力作用。由于流线收缩, 孔喉处流速远大于孔喉前的流速。拉伸流动的特点是速度梯度方向或拉伸速率方向与流动方 向一致。应当指出小分子溶液通过收缩孔喉时,不产生拉伸流动。一般而言,聚合物拉伸粘 度越大,则在流动过程中通过孔喉愈困难,更有利于提高阻力和残余阻力系数。大分子流体 反抗拉伸应力,溶液反抗拉伸产生与流动方向相垂直的法向力,即力图恢复本来的卷曲形态, 从而产生横向力,称为法向力,因此拉伸流动也可以描速流体的粘弹性<sup>[1,2]</sup>。粘弹性与分 子的柔曲性直接有关,链的柔曲性愈大,粘弹性愈显著,HPAM 是具有粘弹性的分子。刚性 分子不存在粘弹性,在外力作用下,分子不改变构象。当外力超过分子链的承受能力时,链 断裂。功能型聚合物分子由于在合成过程添加了功能性单体,使聚合物的拉伸流变性发生明 显变化。

本文用现代分析方法系统分析了大港油田注入污水无机离子、有机分子、三种细菌的 组成,研究了污水中主要活性成分对聚合物分子的降解机理及对聚合物溶液黏度的影响。介 绍了 HAAKE CaBER1 拉伸流变仪的工作原理。用拉伸流变仪研究了几种典型驱油用聚合物 溶液的拉伸流变特性,以及不同水质对聚合物溶液拉伸黏度的影响。

#### 1 实验部分

#### 1.1 化学试剂和仪器

直链型聚合物(63026)的相对分子质量是 2200 万,水解度为 21.2%; 10203 是相对分子 质量为 1700 万的功能型聚合物,水解度为 24.2%。KY-2 是相对分子质量为 2500 万,水解 度为 23.5%的耐温抗盐型聚合物。用矿化度为 2×10<sup>4</sup>mg/L 的注入污水、模拟污水及蒸馏水配 制聚合物。功能型聚合物与聚丙烯酰胺分子相比,它的支链上具有一定活性和高位阻的基团。 用污水配制聚合物溶液扫描电镜图片表明,分子在高矿化度下不易卷曲,以更为舒展的形态存在,因此表现出良好的耐温抗盐性。在85℃条件下,用德国 HAAKE 公司生产的 RS-600型流变仪,研究了聚合物的流变性。在25℃条件下,用德国 HAAKE 公司生产的 HAAKE CaBER1 拉伸流变仪测试;聚合物溶液的浓度,1500mg/L。用 Dionex ICS-1000(Ion Chromatography System of U.S.A)分析了水中无机离子;色谱-质谱仪 6890GC/5973MSD 等仪器分析了水中有机化合物。

#### 1.2 HAAKE CaBER1 拉伸流变仪工作原理

聚合物溶液拉伸流变的测试过程如下图所示,首先把一定浓度的聚合物溶液加入到测试 仪器的上板和下板之间的空间中(图 1a),然后迅速的提升上板到一定高度(图 1b,图 1c), 然后通过激光测量仪不断的测量聚合物丝线中间直径(Dmid)随时间的变化,直至丝线断 裂(图 1e),然后即可以得到直径(Dmid)一时间(time)曲线。由 Dmid-time 曲线,经 过数据处理即可得到 Dmid(t),根据拉伸流变相关机理(见公式),即可算出拉伸应变和拉伸 黏度的数值。

$$\eta_{aap}(\varepsilon) = K\sigma \frac{dt}{dD_{mid}(t)}$$
;  $\varepsilon = \ln(\frac{D_O}{D_{mid(t)}})$ 

其中: K- 参数; σ-表面张力; ε-拉伸应变; η<sub>aap</sub>-拉伸黏度



Fig.1 The test principle of the extensional rheometer

#### 1.3 油田注入污水水质分析

油田注入水一般是采出液经过一系列分离处理后,达到注入水水质标准后,再作为水驱 用水注入到地层。水驱过程中,注入水与地层中原始地层水混合,还与气体、原油接触,使 无机离子和极性有机化合物溶解到水中。采出液在油-水分离过程中,又加入破乳剂、杀菌 剂等,使油水分离后的污水成分变的很复杂。水中高含量盐和活性物质都对聚合物降解产生 严重影响。

为了研究污水中各种离子,活性物质对聚合物溶液粘度影响。现场采集水样,现场分析

了污水中总铁(Fe<sup>2+</sup>+Fe<sup>3+</sup>)、S<sup>2-</sup>、溶液氧和三种细菌,在实验室检测了污水中其它无机离子。 同时水样被达到北京国家环境检测中心,对污水中有机成分进行了全分析,见表1。

注入污水组成如下 (mg/L): K<sup>+</sup>+Na<sup>+</sup> (7439), Ca<sup>2+</sup>+Mg<sup>2+</sup> (339), Cl (11631), SO<sub>4</sub><sup>2-</sup> (95), HCO<sub>3</sub><sup>-</sup> (732), S<sup>2-</sup> (10), Fe<sup>2+</sup>+Fe<sup>3+</sup> (0.6), 溶解氧 (0.6), 总矿化度 (20236); 腐 生菌 (3 个/ml), 硫酸盐还原菌 (600 个/ml); 有机酚 (0.20), 有机酸 (0.03), 醇 (0.05), 酮 (0.06)。水分析结果表明, 污水中 Ca<sup>2+</sup>, Mg<sup>2+</sup>, S<sup>2-</sup>, Fe<sup>2+</sup>, 有机酚及总的矿化物较高。 属于含较高硫污水, 从注入井井口取得的水样, 有很强的 H<sub>2</sub>S 气味, 经过一段时间暴氧后, 污水变黑。

化合物名称	含量 µg/L	化合物名称	含量 µg/L
脂肪烃	5195.8	二异辛基酞酸脂	5.77
芳香烃	220.2	酸脂类	10.3
3-甲基戊酸	12.8	二甲基环己 3-烯醇	1.56
3-羟基丙酸	3.87	二甲基辛烯醇	16.2
二乙基乙酸	9.77	环己基二烯丁醇	16.4
2-辛烯酸	6.18	醇类	13.4
酚	66.2	环庚酮	2.85
2-甲酚	40.6	2,3-二甲基环戊酮	1.85
4-甲酚	80.8	三甲基环戊烯酮	1.71
2-乙基酚	7.21	二甲基壬烯	2.21
2, 4-二甲酚	1.26	2,3-二甲基环庚烯	19.8
3-甲乙基酚	1.57	环烷或烯烃	32.6
二异丁基酞酸脂	5.21	醛类	11.8
二丁基酞酸脂	12.0	N-甲基苯胺	0.97

Table 1 analysis of organic compound composition for injected water

#### 2 结果与讨论

#### 2.1 模拟污水中无机离子及有机物对聚合物溶液黏度的影响

水溶液中聚合物的降解主要机理是,聚合物发生自由基氧化降解反应<sup>[3,4]</sup>。因为聚合物 在生产过程中产生少量的过氧化物杂质,在有光、氧的条件下,过氧化物极易分解成自由基, 这些自由基进攻聚合物分子发生自由基氧化反应,使聚合物分子链断裂。如果溶液在高温或 存在还原性杂质条件下,就会增加自由基的生成速度,加快了自由基氧化过程,加速了聚合 物降解。以上污水分析可见,污水中含有较高的 Fe<sup>2+</sup>、S<sup>2-</sup>和有机酚等还原物质,并且它们 具有较强的还原性,因此对聚合物溶液粘度有较大的影响。

无机离子对聚合物溶液粘度的影响在于盐中和了聚合物分子基团上的电性。随着中 和程度的增加,基团间的斥力减弱,分子恢复卷曲构象。分子卷曲的同时,将阳离子周 围的溶剂化层水分子挤掉,使分子线团密度增大,自然卷曲状的分子流体力学等价球体 积最小,与溶液接触面积最小,故分子间内摩擦力下降至最低限度,溶液粘度降到最低。 图 2 是水中不同 Fe<sup>2+</sup>离子含量对聚合物溶液粘度的影响,可见 Fe<sup>2+</sup>离子的浓度大于 0.1 mg/L,对聚合物溶液粘度的影响较大了。

水中不同 S<sup>2-</sup>离子含量对聚合物溶液粘度的影响可见 S<sup>2-</sup>离子的浓度越大,对聚合物溶液 粘度的影响也越高,当 S<sup>2-</sup>离子浓度达到 10mg/L 时,就能使聚合物溶液的初级粘度降低 90% 以上。S<sup>2-</sup>离子对聚合物降解的作用机理与 Fe<sup>2+</sup>相似。

根据电解质溶液中路易斯提出离子强度概念和德拜-休克尔(Debye-Huckel)的离子互 吸理论。在无机盐浓度和阴离子相同情况下,二价金属离子溶液的离子强度是一价金属离子 溶液强度的3倍。因此溶液里多价离子越高,聚合物分子中基团间斥力减弱就更大,分子更 趋向于卷曲构象。Fe<sup>2+</sup>和S<sup>2-</sup>除具有较强的还原性,能加速聚合物分子发生氧化自由基反应。 还可能与Fe<sup>2+</sup>离子电子层结构有关,使它能削弱聚合物分子间的排斥力,从而改变聚合物分 子的排列构型。根据极化理论S<sup>2-</sup>离子具有较强变形性,所以S<sup>2-</sup>离子的还原性更强,另外S<sup>2-</sup> 存在,会使R-COO-卷缩,使聚合物分子,在水中舒展不开,降低了聚合物的粘度。Ca<sup>2+</sup>和 Mg<sup>2+</sup>离子除了提高溶液离子强度外,聚合物分子中酰胺基团水解生成羧基,羧基与Ca<sup>2+</sup>和 Mg<sup>2+</sup>相互作用,使聚合物发生部分沉淀。以上这些因素作用的结果,表现为聚合物溶液粘 度的下降。多价离子对聚合物溶液粘度损失的影响顺序为:Fe<sup>2+</sup>>Fe<sup>3+</sup>>S<sup>2</sup>>Ca<sup>2+</sup>>Mg<sup>2+</sup>离子。

污水中有机物全分析结果可知,污水中酚类的在 0.2mg/L。用苯酚模拟污水中酚的含量,研究了溶液中不同苯酚浓度时对聚合物溶液粘度的影响。可见,随着溶液中苯酚浓度增大,对聚合物降解影响越大,表现为溶液粘度降低更大,并且在开始的几天里,酚对聚合物 氧化降解比较大。所以在实际用污水配制聚合物溶液时,应尽量把污水中酚除去。酚类有还 原性,易被氧化为醌。一般认为酚对聚合物氧化降解反应表现出的两重性,即促进作用和抑 制作用,其作用主要取决于它们的化学性质,还与溶液浓度、温度等因素有密切的关系。尤 其在高温情况下,这种促进作用明显<sup>[5]</sup>。



54

#### 2.2 聚合物溶液拉伸直径与拉伸断裂时间

当聚合物溶液在多孔介质中以临界流速以上运移时,溶液中聚合物分子链被拉伸,由流动产生了附加阻力。聚合物链拉伸产生的阻力用拉伸黏度表示,在一定流动条件下,由溶液拉伸黏度产生的流动阻力比剪切黏度产生的阻力大 2-3 个数量级。聚合物在拉伸过程中拉伸直径随时间变化及拉伸直径的断裂时间反映聚合物分子的抗拉伸强度,聚合物拉伸粘度大小,在很大程度上可以反映聚合物溶液的增粘性和粘弹性的高低。

图 3 是三种不同聚合物用蒸馏水配制的聚合物溶液拉伸实验,可见功能型聚合物溶液 的拉伸直径断裂时间最长,抗盐耐温型聚合物拉伸直径断裂时间最短。在三种聚合物溶液拉 伸直径断裂之前,功能型聚合物溶液的拉丝直径最大,说明功能型聚合物抗拉性能更强。在 驱油过程中产生的附加阻力更大,有较强的携油能力,可进一步提高微观驱油效率。



Fig.3 The extensional diameter of 3 HPAM solutions prepared with distilled water at 1500 mg/L versus breakup time

图 4 是功能型聚合物用不同水质配制的聚合物溶液的拉伸直径与拉伸时间的关系曲线, 可见油田注入水对功能型聚合物分子的影响最大,致使拉伸直径和断裂时间都变小。主要是 因为污水中矿化度高以及还有其他活性组分作用的结果;而模拟污水仅矿化度高,不含其它 活性组分,因此,用它配制的聚合物溶液的拉伸直径和断裂时间更长。



Fig.4 the effect of water quality on extensional diameter of functional HPAM solution at  $1500\,{\rm mg/L}$ 

#### 2.3 聚合物溶液拉伸黏度

图 5 是用蒸馏水配制的三种聚合物溶液的拉伸黏度结果,可见功能型聚合物溶液的拉伸黏度随拉伸应变增加的幅度大,而另外两种聚合物溶液的拉伸黏度随应变增加的幅度小。 说明功能型聚合物溶液在拉伸流动过程中,产生的流动阻力更大。图6是用不同水配制的聚 合物溶液拉伸粘度。配制聚合物水的性质对聚合物的拉伸黏度影响特别大,从污水对功能型 聚合物的拉伸粘度影响可见。随着水中矿化度和及其它活性组分增大,结果导致聚合物拉伸 黏度大幅度降低。



Fig.5 the extensional viscosity of 3 HPAM solutions prepared with distilled water at 1500mg/L versus. Hencky strain



Fig.6 the effect of water quality on extensional viscosity of functional HPAM solution at 1500 mg/L

#### 3 结论

分析了官 80 区块注入污水中的各种成分, 污水中 Ca<sup>2+</sup>、Mg<sup>2+</sup>、S<sup>2-</sup>、Fe<sup>2+</sup>及酚含量较高, 属于含较高硫的污水。研究了污水中活性组分对聚合物氧化降解的作用机理。用不同矿化度 和活性组分水配制的功能型聚合物拉伸流变测定结果表明,污水成分对聚合物溶液拉伸流变 影响明显。用蒸馏水配制的 10203、KY-2 和 63026 三种聚合物拉伸流变的测量表明, 功能 型聚合物的拉伸黏度高于其它两种聚合物的。

#### 参考文献

- 李保源(LI Bao-yuan).纺织高校基础科学学报(Basic Sciences Journal of Textile Universities), 1998,11(2):126-128
- [2] 孙焕泉(SUN Huan-quan),张坤玲(ZHANG Kun-ling),陈静(CHEN Jing),等.高分子学报 (Acta Polymerica Sinica).2006,(6):810-814
- [3] 朱麟勇(ZHU Lin-yong), 常志英(CHANG Zhi-ying), 李妙贞(LI Miao-zhen), 等. 高分子材
   料科学于与工程(Polymer Materials Science and Engineering), 2000, 16 (1): 113-116.
- [4] 朱麟勇(ZHU Lin-yong), 常志英(CHANG Zhi-ying),李明宇(LI Ming-yu),等.高分子材料科
   学与工程(Polymer Materials Science and Engineering).2000, 16(2) 112-114.
- [5] 朱麟勇(ZHU Lin-yong), 常志英(CHANG Zhi-ying),马昌期(MA Cang-qi),等.高分子材料 科学与工程(Polymer Materials Science and Engineering).2000, 18 (2) 93-96.

# The effect of water quality on elongational behavior of polymer solution

#### LI Dao shan

(Dagang Petroleum Technology Institute Tianjin 300280)

**Abstract:** The content of inorganic ion, organic compound, and three kinds of bacteria in he injected water in block fault G80 of south Dagang oilfield is analyzed systematically with modern equipments. The mechanism of the effect of the active components in the injected water on polymer oxidative degradation has been studied. The working principle of extensional rheometer is introduced. Elongational behavior of three kinds of typical polymer solution is measured with extensional rheometer. The effect of constituents of water on extensional viscosity is investigated. The results show that extensional viscosity of functional polymer is the highest and tension failure time is the longest. The higher salinity water and active components of water, the lower tension failure time and extensional viscosity of polymer solution made with water is.

Key words: elongational behavior; extensional viscosity; injected water; polymer flooding; functional polymer

## 剪切作用下纳米粘土对聚合物熔体非线性粘弹响应的影响\*

杨红梅 张振威 郑强\*\*

(浙江大学高分子科学与工程学系,杭州,310027)

摘 要 以LDPE/EVA/纳米粘土复合体系做研究模型,考察了剪切作用下,分散良好的纳米粘土对基 体聚合物熔体瞬态粘弹响应的影响。稳态剪切时,在低剪切速率下,纳米粘土的加入使体系第一法向应力 差(*N<sub>I</sub>*)变为负值。同时纳米粘土增加了基体聚合物粘弹性对应力作用史的依赖性,预剪切对基体聚合物 瞬态粘弹响应几乎没有影响,而当加入大于3 wt% 的纳米粘土后,与未受预剪切的样品相比,经预剪切的 复合体系瞬态剪切应力值、应力过冲程度及稳态剪切应力值均明显下降;复合体系预剪切前后的稳态剪切 应力差值随纳米粘土含量的增加而增加,一定剪切速率下*N<sub>I</sub>*对剪切时间(应变)的依赖关系发生明显的变 化;随纳米粘土含量的增加,*N<sub>I</sub>*逐渐由正值变为负值。剪切作用下纳米粘土对聚合物熔体瞬态粘弹响应影 响的可能机理在于:纳米粘土在基体聚合物中剥离分散,或聚合物分子链插层于粘土片层间,形成局部有 序结构,并在剪切作用下排列取向,导致体系熔体非线性粘弹响应呈现特异性。

关键词 粘弹响应,纳米粘土,聚乙烯,纳米复合材料

研究表明,聚合物基纳米粘土复合材料体系熔体表现出独特的动态及稳态剪切流变行 为<sup>[1-8]</sup>:①尽管在低剪切速率时,复合体系稳态剪切粘度随粘土含量的增加而增加,而在高 剪切速率下,复合材料熔体的剪切粘度表现出非粘土含量依赖性,即纳米粘土的加入似乎不 影响体系高剪切速率时的剪切粘度;②剥离(插层)分散良好的纳米粘土使基体聚合物熔体 的动态粘弹行为具有显著的末端"类固"特性;③大振幅振荡剪切使体系中粘土片层取向,从 而使体系末端区"类固"特性弱化<sup>[9]</sup>,这一特性与液晶聚合物的流变行为有某些相似之处。流 动反向(flow reversal)实验已经成功应用于向列态液晶聚合物体系<sup>[10]</sup>,通过考察不同应力 作用史对向列态液晶聚合物瞬态粘弹响应的影响,以研究流动过程的结构演化和松弛。结果 表明,为获取向列态液晶聚合物微观结构信息,这种非线性形变的瞬时响应是比稳态剪切更 有效的方法。

由于聚合物基纳米粘土复合材料中,纳米粘土的良好分散,存在局部有序的片层结构, 使得复合体系的结构与向列态液晶聚合物有某些类似。尽管在对插层型聚丙烯基蒙脱土复合 材料的流动反向实验研究中,也发现了不少有意义的现象<sup>[9,11]</sup>,但相关研究尚待系统和深入。 因此,本论文将考察纳米粘土存在时,聚乙烯基蒙脱土纳米复合材料体系熔体的瞬态粘弹响 应的变化规律,以期得到非线性剪切应变下,流动致体系粒子网络结构演化、或者受限聚合 物分子结构演化的信息,从而更深入了解该类复合体系的微观结构。

#### 1 实验

#### 1.1 实验原料

低密度聚乙烯(LDPE), PE-H-18D075(1C7A), 熔融指数 MI = 7.1 g/10 min(190°C, 2.16 kg), 北京燕山石油化工股份有限公司化工一厂产品; 纳米粘土, 离子交换能力 CEC =

59

90 meq/100g, 纯度 ≥95%, 由十六烷基三甲基溴化铵(70 wt %)与十八烷基三甲基溴化铵 (30 wt %) 混合物共同处理钠基蒙脱土而得,浙江华特化工有限公司产品; 乙烯-醋酸乙烯 共聚物 (EVA), H2020, 熔融指数 MI = 1.6 g/10 min (190°C, 2.16 kg), 新加坡 Polyolefin Co.产品。

#### 1.2 样品制备

复合体系采用两步熔融插层法制备,即先将增容剂 EVA 与纳米粘土复合,再与聚合物 LDPE 复合。熔融插层在双螺杆挤出机(PRISM TES 16 TC, UK)进行,挤出工艺为:料筒 温度 140~180℃,模头温度 170℃,螺杆转速 50 rpm。为了保证所有样品经历相同的热历史, 基体聚合物(LDPE/EVA=77/20 共混物)也在相同的工艺条件下挤出两遍,同时所有样品中 均添加适量抗氧剂,以避免流变实验过程中样品的热氧化。所有样品中,LDPE:EVA 均为 77:20,纳米粘土的含量则分别为:0、1、3、5、7、9 wt%。所得的复合物在 170℃下经热 压机压制成测试样品。

#### 1.3 测试表征

用高级流变扩展系统(Advanced Rheology Expansion System, ARES, Rheometrics Sci. Ltd., USA)进行剪切测试, 以考察体系熔体的粘弹响应。测试在平行板下进行, 温度为 150℃, 样品为直径 25 mm, 厚度 2 mm 的圆片:

- 1. 稳态剪切,剪切速率 0.01~10 s<sup>-1</sup>,顺时针方向施力。
- 2. 瞬态粘弹响应按"Step Rate Test"模式进行,对样品施加的应变过程如下:
  - a) 无预剪切时: 在一定剪切速率下, 对样品施加一定的剪切应变(顺时针方向), 历时 300 s;
  - b) 有预剪切时:在一定剪切速率下,对样品施加一定的剪切应变(顺时针方向),历时 300 s;停止实验,并将样品静置 1800 s;在相同的剪切速率下,对样品再次施加剪切应变(反时针方向),历时 300 s。
- 3. 应变扫描按"Dynamic Strain Sweep Test"模式进行,测试频率 ω= 10 rad/s。

#### 2 结果与讨论

#### 2.1 稳态粘弹响应

弹性,是聚合物熔体粘弹响应的重要特性,而法向应力差则是聚合物熔体弹性的主要表现。聚合物熔体受剪切作用时,通常在和剪切垂直的方向上产生法向应力,其中第一法向应力差 N<sub>1</sub>的定义为:

$$N_1 = \sigma_{11} - \sigma_{22} = \Psi_1 \cdot \dot{\gamma}^2 \tag{1}$$

即

$$\log N_1 = \log \Psi_1 + 2\log \dot{\gamma} \tag{2}$$

式中, $\Psi_1$ 为第一法向应力系数, $\dot{\gamma}$ 为剪切速率。由式(2)可知,若 $\Psi_1$ 与 $\dot{\gamma}$ 无关,则 log $N_1 \sim \log \dot{\gamma}$ 曲线是一斜率为2的直线。本研究组的研究已发现<sup>[12-13]</sup>,所研究的复合体系 样品中,纳米粘土在基体聚合物中分散良好,大部分的纳米粘土呈剥离状,同时仍有部分插 层、局部团聚的结构存在。表明在复合体系中,存在由纳米粘土导致的局部有序结构,这些 结构使聚合物分子受限,从而在剪切作用下呈现独特的粘弹特性,特别是随着纳米粘土含量 的增加,复合体系熔体的弹性大大增加。为此,本实验研究特别关注纳米粘土对体系 $N_i$ 的 影响。

图 1 给出了稳态剪切下,基体聚合物和不同纳米粘土含量复合体系的  $N_1$ 与剪切速率的 关系曲线。结果表明,实验过程中,所有体系的  $N_1$  值似乎均表现出极其相似的剪切速率依 赖性,即在低剪切速率下, $N_1$ 值不变,而当剪切速率增至一临界值(约为 0.2~0.3  $s^{-1}$ )时,  $N_1$ 值开始急剧增加,如图 1 (a)。图 1(a)还表明,体系的  $N_1$ 值似乎与纳米粘土的含量无关, 或稳态剪切时,纳米粘土似乎对体系的弹性影响不大。为了更清晰地观察  $N_1$ 对剪切速率的 依赖关系,分别将图 1(a)所示的  $N_1$ 值取低(<0.2  $s^{-1}$ )及高(>0.2  $s^{-1}$ )剪切速率区的数据 作图,得到如图 1(b)、(c)给出的关系曲线。从图 1(b)可以看出,在低剪切速率区,纳米粘土 的存在,使得复合体系表现出与基体聚合物完全不同的弹性响应:随纳米粘土的加入,体系 逐渐表现出负的第一法向应力差;同时在剪切速率<~0.07  $s^{-1}$ 时, $-N_1$ 的数值随纳米粘土含 量的增加而增加,在~0.07  $s^{-1}$ 时出现极值,随后复合体系 $-N_1$ 的数值随纳米粘土含量的增 加而减少,在~0.2  $s^{-1}$ 左右逐渐向正值转变,且各体系  $N_1$ 的差值也逐渐减小。而高速率(> ~0.2  $s^{-1}$ )稳态剪切时,由图 1(c)可看出,随剪切速率的增加,复合体系的  $N_1$ 逐渐转为正值, 而纳米粘土对体系  $N_1$ 的影响也逐渐减弱,甚至几乎没有影响。图 1(c)还显示,在 $\dot{\gamma}$ =0.2~1

 $s^{-1}$ 范围内,  $\log N_1 \sim \log \gamma$  曲线的斜率为 2, 但  $\gamma$  继续增大,则曲线斜率逐渐偏离 2。

一般而言,柔性聚合物熔体在平行板剪切过程中,其分子链受剪切作用而延伸,达稳态 后,分子链的松弛回复使第一法向应力差 N<sub>1</sub>有使平行板分离的倾向,即,通常聚合物的 N<sub>1</sub> 为正值。但在对向列态液晶聚合物的稳态剪切流变行为研究中发现<sup>[14]</sup>,在较低剪切速率下, 出现负 N<sub>1</sub>值的现象。认为主要原因在于:由于液晶分子中,存在棒状有序结构(director), 使得其在静止状态时呈现非球型的结构,而不象柔性聚合物分子链那样成球型无规线团,则 受剪切后的松弛回复过程中难以产生对平板的分离倾向;另一方面,剪切流动对液晶聚合物 分子中有序结构的影响主要表现为流动使其排列(align)或翻转(tumble),当这种流动致 排列取向后使有序结构尺度变得比初始状态宽时,则导致其 N<sub>1</sub>为负值,表明此时的流动将 导致压缩应力并有使平板"缩拢"的倾向。

61



Fig. 1 The dependence of primary normal force difference,  $N_I$ , on shear rate for the polymer matrix and the composites with different contents of nanoclay at 150 °C



At high shear rate

**Fig. 2** The schemes of nano-clay layers aligning and tumbling induced by shear flow with low or high shear rate

类似地,可以想象,在复合体系中,具有较大径厚比(>100)而剥离(插层)分散良 好的纳米粘土片层同样将导致体系内部微观局部有序结构,剪切作用同样可能使粘土片层沿 应力作用方向排列或翻转。在小剪切速率时,无规分散的片层排列是慢速进行的,并伴随片 层的运动聚合物分子链有逐渐取向的趋势,使得此时粘土对体系 *N*<sub>1</sub>的影响非常明显。同时 受限于片层表面的聚合物分子将制约粘土片层排列的进行,结果使得聚合物分子取向,但粘 土片层有可能不取向, 而相对于初始状态更呈现"立起来"的倾向,使有序结构尺度变大, 导致 N<sub>I</sub> 为负值。而在高剪切速率时,聚合物分子链和片层排列取向很快完成,片层也将呈 现沿应力方向取向,有序性增加,有序结构尺度变小,导致正的 N<sub>I</sub> 值,同时粘土的含量对 体系弹性的影响不明显。图2给出了上述推测过程的简单示意图,但其真实的机理尚待进一 步实验研究证实。

#### 2.2 低剪切速率下体系的瞬态粘弹响应

在一定剪切速率下,对样品施加剪切应变,并记录此过程样品的瞬态应力、N<sub>1</sub>值,可 以进一步考察纳米粘土对复合体系瞬态粘弹响应的影响,得到复合体系剪切过程结构演化信 息。图3给出了基体聚合物及复合体系熔体在0.1 s<sup>-1</sup>剪切速率下剪切过程的瞬态应力响应, 以及剪切史对体系瞬态剪切应力的影响关系。可以看出,当未经预剪切时,基体聚合物表现 出非常不明显的应力过冲(overshoot),但随着纳米粘土的加入,特别是当粘土含量大于3 wt % 时,复合体系表现出与基体完全不同的瞬态剪切应力响应,随纳米粘土含量的增加,应 力过冲程度增加,最大应力值也越来越高,由基体的不足1000 MPa (图3(a))增加到9 wt % 粘土含量复合体系的约2500 MPa (图3(f))。

当对样品施加预剪切后,可以发现纳米粘土的加入,大大增加了体系粘弹响应的应力作 用史依赖性。对于基体聚合物而言,应力作用史对其瞬态应力几乎没有影响,预剪切前后, 体系呈现几乎一致的瞬态应力响应,无论是应力过冲程度、最大应力值,还是稳态应力值都 几乎没有变化,表明在历经本实验的静置时间(1800*s*)后,具有柔性分子链的聚合物结构 已完全松弛,并回复至初始状态。添加了少量纳米粘土(1 wt %)后,体系的瞬态粘弹响应 变化不是很明显,但当粘土含量大于 3 wt % 时,复合体系预剪切后的瞬态应力值均小于未 经预剪切样品的相应值,即使达稳态后,应力亦无法恢复到未经预剪切样品的相应值。同时 预剪切前后体系稳态剪切应力差随粘土含量增加而几乎成线性增加,如图(4)所示,显示出 纳米粘土含量越高,复合体系在经预剪切后,其结构越难松弛回复到初始状态。

以 0.1 s<sup>-1</sup> 剪切速率预剪切 300 s 后, 施加给样品的应变已达到 30 strain unit, 从图 5 给出 的应变扫描结果可以发现, 此时已大大超出了体系的线性粘弹区, 表明预剪切作用已破坏了 体系的原有结构。而历时 1800 s 的静置虽然足以使未加纳米粘土的基体聚合物结构回复, 但却无法使添加了纳米粘土的复合体系结构回复到初始状态, 而是在经历了结构演化后重新 建立了新的结构平衡, 显示出分散良好的纳米粘土对聚合物分子极强的限制作用, 这种作用 可赋予聚合物熔体弹性, 并在粘土含量达一定值后, 使复合体系显示出一定的网络结构特性。

为进一步研究纳米粘土对聚合物熔体弹性的影响,在上述剪切过实验程中同时考察了体系第一法向应力差 N<sub>1</sub> 的变化,如图 6 所示。结果表明,未经预剪切的样品(图 6(a)),随着纳米粘土的添加及含量的增加,复合体系的 N<sub>1</sub> 的时间(应变)依赖性与基体聚合物完全不同。在较短的时间,即较小的应变时,纳米粘土对体系的 N<sub>1</sub> 影响不明显,在刚施加剪切应变时,各体系的 N<sub>1</sub> 值几乎都为零,随着时间的增加,应变增大,无粘土的基体聚合物 N<sub>1</sub>

值增加,并逐渐达到平衡;粘土含量为1 wt %的体系,表现出与基体类似的应变依赖性; 随着粘土含量的增加,体系的 N<sub>1</sub> 值在较大的应变时又逐渐降低,特别是对于粘土含量为 7、 9 wt %的复合体系,其 N<sub>1</sub> 值在某一应变临界点后由 0 转变为负值,并在应变继续增加后, 出现 N<sub>1</sub> 值的振荡。另一方面,当样品经过预剪切后(图 6(b)),所有样品的 N<sub>1</sub> 值对剪切时 间(应变)的依赖性几乎类似:小应变时,N<sub>1</sub>为负值且不随应变增加变化,到临界应变后, N<sub>1</sub>增加,基体聚合物和低粘土含量(<5 wt %)的复合体系出现正的 N<sub>1</sub>值,而高粘土含量 (≥5 wt %)的复合体系 N<sub>1</sub> 值在整个实验应变(时间)范围内均为负值,且在同一应变下, 粘土含量越高的体系其 N<sub>1</sub> 的绝对值越大。表明较高含量的纳米粘土增加了复合体系熔体的 弹性,样品经预剪切后,无规分散的粘土片层在大应变作用下发生取向排列,并且由于粒子 网络或者聚合物分子受限的影响,片层在静止松弛过程中,难以回复到未经剪切时的状态, 使得再次剪切时复合体系(特别是高粘土含量的复合体系)的第一法向应力差在预剪切前后 发生很大的变化,并出现负值。



**Fig. 3** The transient stress response under shear rate of  $0.1 \, s^{-1}$  with and without pre-shear for the polymer matrix d the composites with different contents of nanoclay at 150 °C



Fig. 4 The difference of transient stress at steady state with and without pre-shear for the polymer matrix and the composites with different contents of nanoclay at  $150 \,^{\circ}\text{C}$ 

**Fig. 5** The dependence of storage module G' on strain for the polymer matrix and the composites with different contents of nanoclay at 150 °C

将图 6 所示的每个样品预剪切前后的数据按应变 strain unit =剪切速率×时间换算成 N<sub>1</sub> 的应变依赖关系(图 7),以进一步了解纳米粘土对复合体系弹性的影响,以及各体系弹性 响应对应力作用史的依赖性。由图 7 可知,未经预剪切时,尽管 N<sub>1</sub>的应变依赖性不尽相似, 但所有体系均出现一临界应变值 γ<sub>c</sub>,当应变 γ = γ<sub>c</sub>时,体系 N<sub>1</sub>开始变化(正或负方向增大), 且随粘土含量的增加,该γ<sub>c</sub>值逐渐减小。经与图 5 比较发现,所有体系 N<sub>1</sub>开始变化的γ<sub>c</sub>值 与体系粘弹特性从线性到非线性粘弹响应转变的临界应变值几乎一致。表明相对而言,聚合 物熔体非线性粘弹特性对纳米粘土的添加更为敏感,特别是其含量较高时,尤为明显。



**Fig. 6** The primary normal force difference,  $N_l$ , under shear rate of 0.1  $s^{-l}$  (a) without and (b) with pre-shear for the polymer matrix and the composites with different contents of nanoclay at 150 °C



**Fig. 7** The primary normal force difference,  $N_I$ , under shear rate of 0.1  $s^{-1}$  with or without pre-shear for each sample

#### 2.3. 剪切速率对体系瞬态粘弹响应的影响

可见,纳米粘土对聚合物熔体非线性粘弹响应的影响突出体现在复合体系的  $N_l \sim \gamma$  关系上,则剪切过程中,施加应变的快慢应是不能忽略的因素。为此,选择粘土含量居中(3 wt%)的样品,分别以 0.01、0.05、0.1、0.5、1  $s^{-1}$ 的剪切速率施加剪切应变,历时 300 s,记录过程的瞬态剪切应力及第一法向应力差。同时,在剪切结束后,静置样品 1800 s,再以相同的剪切速率反向剪切,历时 300 s,同样记录过程的瞬态剪切应力及第一法向应力差。



**Fig. 8** The dependence of (a) the transient stress response and (b) the primary normal force difference,  $N_i$ , on the strain under different shear rate at 150 °C for the composite containing 3 wt % nanoclay without pre-shear



Fig. 9 The transient stress response and the primary normal force difference,  $N_I$ , under different shear rate at 150 °C for the composite containing 3 wt % nanoclay without/with pre-shear

不同剪切速率下,未经预剪切样品的瞬态应力、第一法向应力差的应变依赖关系结果如 图 8 所示。可以看出,以不同剪切速率剪切时,体系瞬态应力及第一法向应力差均表现出不 同的应变依赖性,剪切速率不同,瞬态剪切应力出现极大值的应变不一样;在不同剪切速率 下,小应变时, $N_I$ 仍然为 0,仍在线性、非线性转变的临界应变处开始向正值或负值变化方 向。当以极低剪切速率 0.01 s<sup>-1</sup>施加剪切应变时,300 s 后体系受到的总应变为 3 strain unit, 尽管已经达到非线性区,但由于应变的施加速率极慢,使得其瞬态应力和  $N_I$ 均表现出特异 性。图 8 表明,以极低剪切速率 0.01 s<sup>-1</sup>施加剪切应变时,在实验范围内,体系瞬态应力随 应变增加而增加,没有出现应力过冲现象;而  $N_I$ 值仍然在临界剪切应变 $\gamma = \gamma_c$ 后出现突变, 由 0 变为负值,其  $N_I \sim \gamma$ 关系曲线形状与图 7(e)、(f)所示的高含量(7、9 wt %)体系在 0.1 s<sup>-1</sup>时的  $N_I \sim \gamma$ 关系曲线类似。随剪切速率增加,体系瞬态剪切应力过冲现象明显,在高 剪切速率(1 s<sup>-1</sup>)时发现瞬态剪切应力出现多个极大值; $N_I \sim \gamma$ 关系在高剪切速率下也出现 特异性,在 $\gamma_c$ 后, $N_I$ 为正值,且其值远大于其他剪切速率下样品的相应值。

另一方面,在不同剪切速率下预剪切后,粘土含量为3wt%的复合体系熔体瞬态剪切应力和 N<sub>1</sub>的应变依赖关系也发生了变化(图9),在小应变时体系的 N<sub>1</sub>值不再恒定为0,而

67

是低于 0 的负值,同时,在应变大于临界值,预剪切后体系的 N<sub>1</sub> 值均随应变的增加而增加。 特别是以极低(0.01 s<sup>-1</sup>)剪切速率施加剪切应变时,经预剪切后的样品其 N<sub>1</sub> 值与预剪切前 相比有很大的不同,预剪切前后体系 N<sub>1</sub> 的应变依赖性差异非常大;而以极高(1 s<sup>-1</sup>)剪切 速率施加剪切应变时,预剪切前后体系 N<sub>1</sub> 的应变依赖性差异却不是很明显。表明,施加应 变的速率,对体系粘弹响应有较大影响,这可能是与复合体系中粘土片层在不同剪切速率下 运动不一样所致,但具体真实的原因尚待进一步实验研究。

#### 3 结论

剥离分散良好的纳米粘土的加入,使复合体系形成局部有序的微结构,导致了体系熔体 弹性的增加,并在剪切流动下表现出特异的非线性粘弹响应,增加了基体聚合物粘弹性对应 力作用史的依赖性。预剪切对基体聚合物瞬态粘弹响应几乎没有影响,但却使复合体系的瞬 态剪切应力值、应力过冲程度及稳态剪切应力值均明显下降;且预剪切前后,复合体系的稳 态剪切应力差值随纳米粘土含量的增加而增加,一定剪切速率下第一法向应力差(N<sub>1</sub>)对剪 切时间(应变)的依赖关系发生明显的变化;随纳米粘土含量的增加,N<sub>1</sub>逐渐由正值变为 负值。剪切作用下纳米粘土对聚合物熔体瞬态粘弹响应影响的可能机理在于:纳米粘土在基 体聚合物中剥离分散,或聚合物分子链插层于粘土片层间,形成局部有序结构,并在剪切作 用下排列取向,导致体系熔体瞬态粘弹响应呈现特异性。

#### REFERENCES

[1] Krishnamoorti R., Giannelis E. P., Macromolecules, 1997, 30, 4097 ~ 4102

[2] Ren J., Silva A. S., Krishnamoorti R., Macromolecules, 2000, 33, 3739 ~ 3746

[3] Krishnamoorti R., Ren J., Silva A. S., J. of Chem. Phy., 2001, 114, 4968 ~ 4973

[4] Chong Min Koo, Mi Jung Kim, Min Ho Choi, Sang Ouk Kim, In Jae Chung, Journal of Applied Polymer Science, 2003, 88: 152 ~ 535

[5] Ranjit Prasad, Vanja Pasanovic-Zujo, Rahul K. Gupta, et al, Polymer Engineering and Science, 2004, 44:1220 ~1230

 [6] Ranjit Prasad, Rahul K. Gupta, Ferenc Cser, Sati N. Bhattacharya, Journal of Applied Polymer Science, 2006, 101: 2127 ~ 2135

 [7] Defeng Wu, Chixing Zhou, Wei Yu, Xie Fan, Journal of Polymer Science Part B: Polymer Physics, 2005, 43: 2807 ~ 2818

[8] Susmita Sadhu, Anil K. Bhowmick, Journal of Polymer Science Part B: Polymer Physics,
 2005, 43: 1854 ~ 1864

- [9] M.J. Solomon, A.S. Almusallam, K.F. Seefeldt, Macromolecules, 2001, 34:1864~1872
- [10] Lynn M. Walker, Norman J. Wagner, et al, J. Rheology, 1995, 39:925~9520
- [11] Jian Li, Cixing Zhou, Gang Wang, Delu Zhao, J. of Applied Polymer Science, 2003, 89:3609~3617
- [12] YANG Hong-mei, SONG Yi-hu, XU Bo and ZHENG Qiang, Chemical Research Chinese University, 2006, 22 (3): 383 ~ 387
- [13] YANG Hong-mei, DU Miao and ZHENG Qiang, Chemical Research Chinese University, 2006, 22 (5): 651 ~ 657
- [14] Alex M. JAMIESON, Dongfeng GU, F. L. CHEN and S. SMITH, Prog. Polym. Sci., 1996, 21: 981-1033

## The Influences of Nano-clay on Nonlinear Viscoelastic Response

# **Under Shear for Polymer Melts**

Hongmei YANG\*\*, Zhenwei ZHANG and Qiang ZHENG

(Department of Polymer Science and Engineering, Zhejiang University, Hangzhou, 310027)

**Abstract** The influences of nano-clay on nonlinear viscoelastic response for polymer melts were studied by using LDPE/EVA/nano-clay composites as research models. During steady shear, the composites have negative primary normal force difference ( $N_I$ ) at lower shear rates region. It can be found that the dependence of matrix viscoelastisity on the stress histories can be increased by the nano-clay layers dispersed well into polymer matrix. The viscoelastic responses of matrix polymer are independent on the pre-shear. However, for the composites containing 3 wt % or more nano-clay with pre-shear, the values of transient stress, overshoot and steady stress are lower than those of the sample without pre-shear. The differences of transient stress at steady state for the composites with and without pre-shear increase with the contents of nano-clay, and the dependences of primary normal force difference ( $N_I$ ) on time (strain) for the composites with pre-shear differ entirely from those of the samples without pre-shear have positive  $N_I$  instead of negative one with increase of nano-clay content. The possible mechanism of polymer melts viscoelastic response affected by nano-clay should be proposed. It seems that the layers of nano-clay were exfoliated or intercalated by polymer chains, which induce the formation of directors in the polymer matrix. The composites melts show abnormal nonlinear viscoelastic response due to alignment or orientation of directors under shear stress.

Keywords Viscoelastic response, Nano-clay, Polyethylene, Nanocomposites
## 延缓形成粘弹性胶束体系流变动力学性质研究

方 波\*1 卢拥军<sup>1,2</sup> 房鼎业<sup>1</sup> 丁云宏<sup>2</sup> 张汝生<sup>2</sup> 舒玉华<sup>2</sup> 汪永利<sup>2</sup>
 (1、华东理工大学化工学院,上海,200237;
 2 中国石油勘探开发研究院廊坊分院,廊坊,065007)

**摘要**:本文考察了粘弹性胶束清洁压裂液(VES-60)的流变动力学过程。建立 4 参数粘弹性胶束的流 变动力学模型描述粘弹性胶束压裂液的延缓形成过程。结果表明,流变动力学模型能够描述粘弹性胶束的 延缓形成过程,模型计算值和实验值吻合良好,模型参数物理意义合理。

关键词:粘弹性 胶束 表面活性剂 流变动力学 清洁压裂液

#### 1、引言

水力压裂施工是低渗透油气藏改造、提高石油和天然气采收率的重要措施。近年来研究 表明,表面活性剂在一定条件下可形成粘弹性胶束压裂液,具有良好的流变性能,清洁、无 固相残渣,正发展成为新一代清洁压裂液<sup>[1~13]</sup>。国外自 1997 年起,已在美国和加拿大开展 了 400 多井次的清洁压裂任务。该压裂液主要采用瓢儿菜基-2 羟乙基氯化铵为表面活性剂, 以氯化铵、氯化钾、水杨酸钠混合液为盐溶液<sup>[3,6]</sup>。

目前,国内对粘弹性胶束压裂液的研究很少,多为引进国外压裂液体系在国内油田施工的报道。本文以 VES-60 为主要原料,着重研究了粘弹性胶束的形成过程。针对粘弹性胶束形成过程中粘度随时间的变化关系,建立了4参数流变动力学数学模型,并用于描述粘弹性胶束压裂液延缓形成的流变动力学过程,为深入理解胶束形成与体系流变性指标的变化关系奠定基础。对粘弹性胶束延缓形成过程的流变动力学研究尚未见报道。

#### 2、材料和研究方法

#### 2.1 材料和仪器

VES-60 表面活性剂:由 C<sub>16</sub>、C<sub>18</sub>烷基三甲基季铵盐和助剂组成,自制品。

RS-75 控制应力流变仪、RV20 旋转粘度计(德国 Haake 公司)。

将一定体积分数的表面活性剂 VES-60 加入到去离子水中,迅速混合均匀,添加到流变 仪中。在一定温度和剪切速率下,记录体系粘度和剪切应力随时间的变化关系,获得胶束形 成过程的流变动力学曲线。

#### 3、粘弹性胶束形成流变动力学模型的建立

#### 3.1 粘弹性胶束的形成

<sup>1)</sup> 课题来源:国家973项目,编号: 2001CB209107;国家自然科学基金项目,编号: 20276016;上海市高 等学校青年科学基金项目,01QN28。\* 通讯联系人。

表面活性剂为两亲分子,由其形成的粘弹性胶束结构与高分子溶液产生粘弹性有所不同。前 者是小分子溶液按照体系能量最低原理组成一定的结构体,如球型胶束和棒状胶束等。研究 表明,表面活性剂溶液之所以产生粘弹性,主要伴随着胶束结构从球型胶束转变为棒状胶束。 粘弹性胶束的形成需要一定的时间和能量。本文对 VES 粘弹性胶束体系的形成过程进行研 究,着重考察了胶束形成过程中体系的粘度随时间变化过程,获得了胶束形成过程中的流变 动力学信息,为进一步建立流变动力学模型表征胶束形成过程奠定基础。为说明问题,典型 的 VES 粘弹性胶束形成过程的流变动力学曲线如图 1 所示<sup>[13]</sup>。



图 1 4%VES 胶束形成过程流变动力学曲线(10s<sup>-1</sup>)

由图 1 可见,粘弹性胶束的形成需要一定的时间。随时间的增加,胶束体系的粘度逐渐 增大,并达到最大平衡值。图 1 中表现出两种形式的胶束形成过程。第一种形式为:胶束体 系的粘度随时间迅速增加,并最终达到平衡值;第二种形式为随时间的增大,胶束体系的粘 度变化十分缓慢,当达到某一临界时间时,胶束体系的粘度才开始增大,并逐渐达到平衡值。 Oelschlaeger 等在研究含氟阳离子表面活性剂溶液在低离子强度下的粘度随时间的变化关系 时,也观察到了类似的现象<sup>[14]</sup>。

第一种形式的胶束形成动力学过程,可以看作是第二种的特殊情况。对不同体系,胶束 开始形成的时间和开始形成的粘度各不相同,主要与体系的初始能量有较大关系。从图 1 中可见,体系温度为 10 度时,需要经过 1600s 才开始逐渐形成粘弹性胶束;而在体系温度 为 20 度时,则需要经过 254.77s 才开始形成粘弹性胶束,且形成速度明显大于 10 度的体系。 当体系温度大于 30 度时,胶束可立即形成,而且胶束结构逐渐加强。

本文针对胶束延缓形成过程建立流变动力学模型,描述粘弹性胶束形成的流变动力学过程。

#### 3.2 4-参数粘弹性胶束形成流变动力学模型的建立

流变动力学旨在揭示体系的结构和流变特性随时间的变化关系,建立结构与流变性变化

之间的相互关系。

伴随结构的变化,体系的流变学参数相应变化。所以,流变动力学的核心为体系的结构 变化动力学,可利用体系结构变化的规律来揭示流变动力学过程。

对粘弹性胶束形成而言,伴随着从球型胶束到棒状胶束的变化过程。假设粘弹性胶束形成过程等价于下列结构变化过程:

#### $A \rightarrow B$

假设 A 为球型胶束, B 为棒状胶束;由于球型胶束体系的粘度与溶剂水的粘度相当, 所以体系的粘度主要是由棒状胶束贡献的。假设体系的粘度与棒状胶束 B 的浓度成正比。

初始时刻,A的浓度为CA0,t时刻A的浓度为CA

假设A的消耗速度符合一级反应:

$$-\frac{dC_A}{dt} = kC_A \tag{1}$$
$$t = 0, C_A = C_{A0}, \ \eta = \eta_0$$

式中: k为结构变化速率常数,  $\eta_0$ 为体系的初始粘度。

积分可得: 
$$C_A = C_{A0} \exp(-kt)$$
 (2)

则: 生成胶束 B 消耗的 A 量为 ( $C_{40} - C_A$ )

假设t时刻体系粘度相对于初始粘度的增量与A组分减少的量呈正比,即:

$$\eta(t) - \eta_0 = K(C_{A0} - C_A) = KC_{A0}[1 - \exp(-kt)]$$
(3)

式中: K 为比例系数。

若所有的 A 全部生成 B,则 C<sub>A0</sub> 对应于 B 的最大浓度 C<sub>Bmax</sub>, KC<sub>A0</sub>等于体系的最大粘度增量( $\eta_{max} - \eta_0$ ),则体系的流变动力学方程为:

$$\eta(t) - \eta_0 = KC_{A0}[1 - \exp(-kt)] = (\eta_{\max} - \eta_0)[1 - \exp(-kt)]$$
(4)

该流变动力学方程含有 $\eta_{max}$ 、 $\eta_0$ 和k共三个参数。

对第二种胶束形成流变动力学过程,可将式-(4)写成分段函数,修正为:

$$\eta(t) = \eta_c \qquad (t \le t_c) \qquad (5-a)$$

$$\eta(t) - \eta_c = (\eta_{\max} - \eta_c) \{1 - \exp[-k(t - t_c)]\} \qquad (t \ge t_c)$$
(5-b)

式中: $t_c$ 为胶束开始形成的时间,s; $\eta_c$ 为胶束开始形成时体系的粘度,Pa.s;此两个参

数由实验确定。式-(5)即为4参数流变动力学方程,用于描述延缓形成胶束体系的流变动力学过程。

4. 结果与讨论

#### 4.1 不计延缓时间的粘弹性胶束形成过程模拟

粘弹性胶束的形成过程中伴随着胶束结构的复杂变化,流变动力学主要揭示流变学性质 与结构的之间的动态变化关系。作为对比,首先不考虑延缓时间,尝试用4参数流变动力学 模型描述粘弹性胶束的形成过程,结果分别如图2-图4所示,模型参数示于表1中。



图 2 用 4 参数流变动力学方程模拟 4%VES 粘弹性胶束形成过程 (20 度)



图 4 用 4 参数模型描述 2% VES 粘弹性胶束 形成流变动力学过程 (30 度)



图 3 用 4 参数模型模拟 2% VES 粘弹性胶束 形成流变动力学过程 (40 度)



图 5 用 4 参数模型描述 4% VES 粘弹性胶束 形成流变动力学过程 (20 度)

Cs/%	T/℃	$\eta_{ m max}$ /Pa.s	k /s <sup>-1</sup>	<i>t<sub>c</sub></i> /s	$\eta_c$ /Pa.s	残差
4% VES-60	20	2.431	6.765×10 <sup>-4</sup>	18.408	0.0664	$1.545 \times 10^{-1}$
2% VES-60	40	0.178	1.468×10 <sup>-3</sup>	12.308	0.0345	2.323×10 <sup>-2</sup>
2% VES-60	30	1.589	1.207×10 <sup>-3</sup>	24.465	0.0793	9.580×10 <sup>-2</sup>

表1 不考虑延缓时间的粘弹性胶束形成过程模拟参数

Cs: the concentration of VES-60 in the samples,%; T: temperature, °C;  $t_c$ : the time when the viscoelastic micelle system begin to form steadily,s;  $\eta_c$ : the viscosity of viscoelastic micelle system begin to form steadily,Pa.s; k: Structure changing rate constant, s<sup>-1</sup>;  $\eta_{max}$ : the maximum viscosity of viscoelastic micelle system, Pa.s; 残差 为模型计算与实验值之差的方均根。 由图 2、图 3 和图 4 可见,用 2 参数流变动力学方程描述胶束形成流变动力学过程时,如果不计胶束延缓形成时间,则在胶束未形成的初始阶段和形成阶段,计算值和实验值偏差较大,说明延缓形成时间必须充分考虑。

#### 4.2 用4参数流变动力学方程描述粘弹性胶束延缓形成过程

考虑延缓时间,用4参数模型描述胶束延缓形成过程。分别对20度下4%VES粘弹性 胶束形成过程、40度下2%VES粘弹性胶束形成过程和30度下2%VES粘弹性胶束形成过 程进行模拟,计算结果分别如图5~图7所示,模型参数列于表2中。



由图 5-图 7 可知,在胶束开始形成后的过程中,模型计算值与实验值吻合。说明建立的流变动力学模型反映了胶束延缓形成过程中的主要影响因素,从而能够较好地揭示胶束形成的流变动力学过程。

Cs/%	T/℃	$\eta_{ m max}$ /Pa.s	k /s <sup>-1</sup>	<i>t<sub>c</sub></i> /s	$\eta_{c}$ /Pa.s	残差
4% VES-60	20	1.716	1.878×10 <sup>-3</sup>	254.77	0.0746	6.8493×10 <sup>-2</sup>
2% VES-60	40	0.159	3.434×10 <sup>-3</sup>	242.609	0.0396	1.6422×10 <sup>-2</sup>
2% VES-60	30	1.068	4.428×10 <sup>-3</sup>	194.13	0.105	3.6527×10 <sup>-2</sup>

表 2 4 参数流变动力学方程描述粘弹性胶束压裂液流变动力学过程的模型参数

Cs: the concentration of VES-60 in the samples,%; T: temperature, °C;  $t_c$ : the time when the viscoelastic micelle system begin to form steadily,s;  $\eta_c$ : the viscosity of viscoelastic micelle system begin to form steadily,Pa.s; k: Structure changing rate constant, s<sup>-1</sup>;  $\eta_{max}$ : the maximum viscosity of viscoelastic micelle system, Pa.s; 残差 为模型计算与实验值之差的方均根。

进一步对比图 6、图 7 和表 2 中相应的模型参数可知,2%的 VES 在 30 度下形成胶束的 速度明显高于其在 40 度下形成胶束的速度。因此,2%的 VES 在 30 度下的结构变化速率常 数 k 大于其在 40 度下的结构变化速率常数;另外可以看出, η<sub>max</sub>的模拟结果合理,证明所 建立的流变动力学方程的参数物理意义明确、合理,可描述粘弹性胶束的形成过程。

74

#### 1.4、结论

针对粘弹性胶束压裂液的延缓形成过程中粘度随时间的变化关系,首次建立 4 参数流 变动力学模型描述胶束延缓形成过程。结果表明,该流变动力学模型简捷实用,模型计算值 与实验值吻合良好,参数意义明确,能够较确切地描述具有延缓形成胶束过程的流变动力学, 为拓展流变动力学的应用研究奠定基础。

#### 参考文献

[1] Qu Qi, Nelson E B, Willberg DM,et al. Compositions containing aqueous viscosifying surfactants and methods for applying such compositions in subterranean formations [P]. U.S. Patent 6,435,277, August 20, 2002

[2] Samuel M M, Card R J, Nelson E B,etal. Polymer-free fluid for fracturing applications[J]. SPE Drill. & Completion, 1999,14(4): 240-245

[3] 卢拥军, 汪永利, 方波, 等.粘弹性胶束流体流变特性及其工程应用[B].2002 流变学进展, 中国科学技术出版社, 北京, 2002: 46-52

[4] 卢拥军,方波,房鼎业,等. 粘弹性表面活性剂胶束体系及其流变特性[J].油田化学,2003, 16(3): 291—294

[5] 卢拥军,方波,房鼎业,等.粘弹性胶束压裂液的形成与流变性质[J].油田化学,2003, 20 (4): 327-330

[6] Chase B, Chmilowski W, Dang Y,et al. Clear fracturing fluids for increased well productivity. Oilfield Review, 1997,20-33

[7] 郭拥军,李健.粘弹性表面活性剂溶液及其在油田中的应用潜力.日用化学品科学,1999, (4):29-33

[8] Gino F D, Philip J R, Ahmad J K. Well service and method of making and using the same[P].U.S. Patent 2002/0189810A1, Dec. 19, 2002

[9] Matthew J M, Matthew S, Palathinkara S V, et al. Compositions and methods to control fluid loss in surfactant-based wellbore service fluids[P]. U.S. Patent 2002/0169085A1,Nov.14,2002

[10] Kelven W E, Curtis L B, Matthew J M. Methods for stimulating hydrocarbon production [P].

U.S. Patent 2003/0054962A1, Mar. 20, 2003

[11] Zhou Jian, Hughes T. Viscoelastic compositions [P]. WO 02/064945 A1, Aug. 22, 2002

[12] Hughes T, Jones T, Gareth J, et al. Aqueous Viscoelastic fluid [P]. WO 02/064947 A1,Aug.22,2002

[13] Manilal S D, Jiang Y. Viscoelastic surfactant fluids and related methods of use [P]. U.S. Patent 2003/004-546A1,Feb.14,2003

[14] Oelschlaeger C, Waton G, Buhler E, et al. Rheological and light scattering studies of cationic fluorocarbon solutions at low ionic strength. Langmuir,2002,18(8):3076-3085

# Study on the Rheological Dynamics for the Delayed Formation of Viscoelastic Micelle Systems

Fang Bo<sup>\*1</sup> Lu Yongjun<sup>1, 2</sup> Fang Dingye<sup>1</sup> Ding Yunhong<sup>2</sup> Zhang Rusheng<sup>2</sup>

Shu Yuhua<sup>2</sup> Wang Yongli<sup>2</sup>

 East China University of Science and Technology, Shanghai ,200237;
 Langfang Branch, Research Institute of Petroleum Exploration and development, Langfang, 065007)

**Abstract:** The rheological dynamics for the formation of clear viscoelastic micelle fracturing fluids (VES-60) were investigated. The 4-parameter rheological dynamics model and equations were established firstly, and was applied to simulate the delayed formation of clear viscoelastic micelles fracturing fluids. The results showed that, the rheological dynamics equation can be applied to describe the delayed formation of viscoelastic micelle systems correctly, the calculated data were in good agreement with the experimental data, and the meanings of the model parameters were reasonable.

Keywords: Viscoelasticity, Micelles, surfactant, Rheological dynamics, Clear fracturing fluids

## 最小耗能原理及其在流变固体中的应用

罗迎社<sup>1</sup>, 唐松花<sup>2,3</sup>, 周筑宝<sup>2</sup>

# 1.中南林业科技大学流变力学与材料工程研究所,长沙,410004 2.中南大学土木建筑学院,长沙 410075 3.湘潭大学基础力学与材料工程研究所,湘潭 411105

摘要:本文简要地介绍了一个具有新内涵的最小耗能原理并讨论了它在流变固体力学中的应用。文中根据基于最小耗能原理的本构关系理论,导出了 Bingham 体及 Maxwell 体的本构关系;根据基于最小耗能原理的最小功耗原理,建立了准静态粘弹性力学率型变分原理的两种基本型式。文中所举的两个算例表明,根据上述新变分原理的两种基本型式,都能求得问题的正确解答。

关键词:最小耗能原理;流变固体;本构关系;变分原理。

Abstracts: A least energy dissipation principle with new intension was introduced and discovered on its application in the rheological solid mechanics. According to the constitutive relation theory based on the least energy dissipation principle, the constitutive relation of Bingham body and Maxwell body were deduced; According to the least work consumption principle based on the least energy dissipation principle, two basic kinds of variational principle of quasistatic visco-elastic mechanics were established. It is shown from two examples that the correct solutions of the problems can be gained according to the two basic kinds of new variational principle above.

Keywords: The least energy dissipation principle; rheological solid; constitutive relation; variational principle.

#### 1 关于最小耗能原理

现有的最小能耗原理(最小能耗率,最小能量)原理的理论基础是非平衡态热力学中的 最小熵产生原理。由于最小熵产生原理只适用于平衡态附近线性区的稳定态(平衡态可看作 是稳定态的一种特例),所以现有的最小能耗原理也只能是在同样严格的限制条件下才成立。 即系统只有在边界条件恒定的情况下,在平衡态附近的线性区内达到稳定时,才具有耗能率 最小的结论<sup>[1~6]</sup>。

文献 [7,8] 借助于缩小寻找最小值范围的方法,证明了一个具有新内涵的最小耗能原 理。即"任何耗能过程,都将在与其相应的约束条件下,以最小耗能的方式进行"(这里所谓 的"耗能",是指能量的转换与传输;这里所谓的"相应的约束条件",是指过程所应满足的控 制方程和定解条件;这里所谓的"以最小耗能的方式进行",是指在耗能过程中的任意瞬时, 系统的耗能率都取当时所有可能耗能率中的最小值)。由于这个具有新内涵的最小耗能原理, 实际上已将现有的最小能耗原理从一个只在平衡态附近线性区的稳定态才成立的结论,拓展 成为一个在非线性非平衡态热力学过程中的任意瞬时都成立的结论,从而使它具有了普遍意

77

)

义。显然,由于这个具有新内涵的最小耗能原理的加入,将使目前已广泛应用于各学科领域的能量原理更趋完善。

本文仅讨论这个新原理在流变固体力学中的应用。所谓"流变固体",通常是指松弛时间 比观察时间更长的一类流变体。流变固体力学涵盖着粘弹性力学,粘塑性力学,粘弹塑性力 学等分支学科,而弹性力学,塑性力学则可视为它的特例。

#### 2 由最小耗能原理导出 Bingham 体和 Maxwell 体的本构关系

文献[7]建立了一种基于最小耗能原理的本构关系理论。下面应用这种新理论来建立 流变学中常用的 Bingham 体和 Maxwell 体的本构关系。众所周知,它们分别是最简单,最 具代表性的粘塑和粘弹体。

对于 Bingham 体,可设应力张量主轴与不可逆流变应变率张量主轴重合<sup>[9]</sup>。如此,当 只存在不可逆流变应变一种耗能机制时,Bingham 体微小单位体积的耗能率

$$\varphi = \sigma_i \dot{\varepsilon}_i^R \tag{1}$$

其中 $\sigma_i$ ,  $\dot{\varepsilon}_i^R$  (*i* = 1,2,3) 分别为主应力和不可逆流变应变率。因为 Bingham 体只有在屈服之后 才会发生不可逆流变应变,所以以(1)式表示的"耗能"只有在屈服条件得到满足的情况下 才会发生。因此屈服条件可视为是以(1)式表示的耗能过程的"相应的约束条件",即只有 在满足屈服条件(例如 Mises 屈服条件)之后,以(1)式表示的耗能过程才会发生。于是 根据最小耗能原理,(1)式应在满足

$$F(\sigma_{i}) = \sigma_{1}^{2} + \sigma_{2}^{2} + \sigma_{3}^{2} - \sigma_{1}\sigma_{2} - \sigma_{2}\sigma_{3} - \sigma_{3}\sigma_{1} - \sigma_{s}^{2} = 0$$
(2)

的条件下取驻值((2)式中的 $\sigma_s$ 为 Bingham 体中摩擦件的材料参数,即屈服应力)。综上, 在引入 Lagrange 乘子之后有

$$\begin{cases} \dot{\varepsilon}_{1}^{R} + \sigma_{1} \frac{\partial \dot{\varepsilon}_{1}^{R}}{\partial \sigma_{1}} + \sigma_{2} \frac{\partial \dot{\varepsilon}_{2}^{R}}{\partial \sigma_{1}} + \sigma_{3} \frac{\partial \dot{\varepsilon}_{3}^{R}}{\partial \sigma_{1}} + \lambda \left(2\sigma_{1} - \sigma_{2} - \sigma_{3}\right) = 0 \\ \dot{\varepsilon}_{2}^{R} + \sigma_{2} \frac{\partial \dot{\varepsilon}_{2}^{R}}{\partial \sigma_{2}} + \sigma_{1} \frac{\partial \dot{\varepsilon}_{1}^{R}}{\partial \sigma_{2}} + \sigma_{3} \frac{\partial \dot{\varepsilon}_{3}^{R}}{\partial \sigma_{2}} + \lambda \left(2\sigma_{2} - \sigma_{1} - \sigma_{3}\right) = 0 \\ \dot{\varepsilon}_{3}^{R} + \sigma_{3} \frac{\partial \dot{\varepsilon}_{3}^{R}}{\partial \sigma_{3}} + \sigma_{1} \frac{\partial \dot{\varepsilon}_{1}^{R}}{\partial \sigma_{3}} + \sigma_{2} \frac{\partial \dot{\varepsilon}_{2}^{R}}{\partial \sigma_{3}} + \lambda \left(2\sigma_{3} - \sigma_{1} - \sigma_{2}\right) = 0 \end{cases}$$
(3)

(3) 式是以 $\sigma_i$ 为自变量的关于 $\dot{\varepsilon}_i^R$ 的一阶偏微分方程组(i = 1, 2, 3)。可以验证:

$$\begin{cases} \dot{\varepsilon}_{1}^{R} = \frac{1}{\eta} \left\{ (\sigma_{1} - \sigma_{s}) - \frac{1}{2} [(\sigma_{2} - \sigma_{s}) + (\sigma_{3} - \sigma_{s})] \right\} \\ \dot{\varepsilon}_{2}^{R} = \frac{1}{\eta} \left\{ (\sigma_{2} - \sigma_{s}) - \frac{1}{2} [(\sigma_{1} - \sigma_{s}) + (\sigma_{3} - \sigma_{s})] \right\} \\ \dot{\varepsilon}_{3}^{R} = \frac{1}{\eta} \left\{ (\sigma_{3} - \sigma_{s}) - \frac{1}{2} [(\sigma_{1} - \sigma_{s}) + (\sigma_{2} - \sigma_{s})] \right\} \end{cases}$$
(4)

就是(3)式当其中的 $\lambda$ 取为 $-\frac{1}{\eta}$ 时的解答。另由模型理论<sup>[10]</sup>可知, Bingham 体在单向应

力状态下的本构关系为
$$\dot{\varepsilon}^{R} = -\frac{1}{\eta} (\sigma - \sigma_{s}) ( \exists \sigma < \sigma_{s} \text{时} \dot{\varepsilon}^{R} = 0 )$$
,其中 $\eta$ 为 Bingham 体粘壶的粘性系数。由于可设粘性应变的 Poisson 比 $\mu = \frac{1}{2}$ ,故按模型理论的结果  
 $\dot{\varepsilon}^{R} = -\frac{1}{\eta} (\sigma - \sigma_{s})$ 及叠加原理推得的,Bingham 体在复杂应力状态下的本构关系也是(4)式。这表明由最小耗能原理导出的(4)式,就是复杂应力状态下 Bingham 体的本构关系。

令(4)式中的 $\sigma_s = 0$ (这相当于假设 Bingham 体中的粘壶没有并联摩擦件的情况), 就可得到复杂应力状态下 Maxwell 体的不可逆流变应变率

$$\begin{cases} \dot{\varepsilon}_{1}^{R} = \frac{1}{\eta} \bigg[ \sigma_{1} - \frac{1}{2} (\sigma_{2} + \sigma_{3}) \bigg] \\ \dot{\varepsilon}_{2}^{R} = \frac{1}{\eta} \bigg[ \sigma_{2} - \frac{1}{2} (\sigma_{1} + \sigma_{3}) \bigg] \\ \dot{\varepsilon}_{3}^{R} = \frac{1}{\eta} \bigg[ \sigma_{3} - \frac{1}{2} (\sigma_{1} + \sigma_{2}) \bigg] \end{cases}$$

$$(5)$$

于是由(5)式可得 Maxwell 体在复杂应力状态下的本构方程为

$$\begin{cases} \dot{\varepsilon}_{1} = \dot{\varepsilon}_{1}^{e} + \dot{\varepsilon}_{1}^{R} = \frac{1}{E} [\dot{\sigma}_{1} - \mu (\dot{\sigma}_{2} + \dot{\sigma}_{3})] + \frac{1}{\eta} \bigg[ \sigma_{1} - \frac{1}{2} (\sigma_{2} + \sigma_{3}) \bigg] \\ \dot{\varepsilon}_{2} = \dot{\varepsilon}_{2}^{e} + \dot{\varepsilon}_{2}^{R} = \frac{1}{E} [\dot{\sigma}_{2} - \mu (\dot{\sigma}_{1} + \dot{\sigma}_{3})] + \frac{1}{\eta} \bigg[ \sigma_{2} - \frac{1}{2} (\sigma_{1} + \sigma_{3}) \bigg] \\ \dot{\varepsilon}_{3} = \dot{\varepsilon}_{3}^{e} + \dot{\varepsilon}_{3}^{R} = \frac{1}{E} [\dot{\sigma}_{3} - \mu (\dot{\sigma}_{1} + \dot{\sigma}_{2})] + \frac{1}{\eta} \bigg[ \sigma_{3} - \frac{1}{2} (\sigma_{1} + \sigma_{2}) \bigg]$$

$$(6)$$

其中 $\dot{\varepsilon}_i^R$ 为主弹性应变率, $\dot{\sigma}_i$ 为主应力变化率(i = 1, 2, 3),  $E, \mu$ 分别为弹性元件的弹性模量和 Poisson 比。对于单向应力状态,由(4)式和(6)式可得 Bingham 体和 Maxwell 体的本构关系为

$$\dot{\varepsilon}^{R} = -\frac{1}{\eta} \left( \sigma - \sigma_{s} \right) \tag{7}$$

及

$$\dot{\varepsilon} = \frac{1}{E}\dot{\sigma} + \frac{1}{n}\sigma \tag{8}$$

显然,它们与由模型理论所得结果完全一致,这样就从最小耗能原理导出了 Bingham 体和 Maxwell 体的微分型本构关系。如所周知,根据叠加原理,还可由微分型本构关系推得与之 相应的积分型本构关系。

#### 3 基于最小耗能原理的最小功耗原理

文献[8]从最小耗能原理出发,导出了一个可以包含能量耗散项在内的新极值原理—— 最小功耗原理,即"任何作用于系统的外力功消耗过程,都将在与其相应的约束条件下,以 消耗外力功最小的方式进行。"这里所谓的"外力功消耗"(或"消耗外力功")是指作用于系统的 外力功被转换为系统的势能、动能及耗散能;这里所谓的"以消耗外力功最小的方式进行", 是指在外力功消耗过程中的任意瞬时,其外力功的消耗率(简称"功耗率")都取当时所有可能 外力功消耗率中的最小值;这里所谓的"相应的约束条件",是指在外力功消耗率的表达式中 包含的物理量所应满足的控制方程(即基本方程)和定解条件。于是根据上述基于新最小耗能 原理的最小功耗原理,各类力学问题(无论其是否需要考虑能量耗散)的变分原理,都可用在 满足所讨论问题的基本方程及定解条件下的、使外力功率(即"功耗率")泛函表示式取最小值 的条件变分问题的形式给出。

综上,最小功耗原理又可表述为:各类力学问题的真实(正确)解答(即满足所讨论问题全部基本方程和定解条件的解答),都必使

$$\delta \dot{W} = \delta (\iiint_{v} F_{i} \dot{u}_{i} dv + \iint_{S_{p}} \overline{P_{i}} \dot{u}_{i} ds) = 0 \qquad (9)$$

或使与(9)式等价的

 $\delta \dot{U}_H + \delta (\dot{U}_s - \dot{T}) = 0 \qquad (10)$ 

 $\delta \dot{W} - \delta \dot{U}_H - \delta (\dot{U}_s - \dot{T}) = 0 \quad (11)$ 

中的任一式成立。其中 $\dot{W}$ 为总外力功率, $F_i$ 、 $\overline{P_i}$ 分别为外力中的体力和面力分量, $\dot{u_i}$ 为位 移分量的变化率(*i*=1, 2, 3); $\dot{U}_H$ 为总能量耗散率; $\dot{U}_s$ 为总势能变化率; $\dot{T}$ 为总动能变化率。

#### 四. 基于最小功耗原理的准静态粘弹性力学率型变分原理

1. 准静态各向同性小变形情况下粘弹性力学问题的基本方程及定解条件:

粘弹性力学与弹性力学及塑性力学基本方程的区别,仅在于它们的本构方程不同。因此, 准静态各向同性小变形情况下粘弹性力学问题的基本方程及定解条件为:

平衡方程: 
$$\sigma_{ii,i}(t) + F_i(t) = 0$$
 (12)

几何方程: 
$$\varepsilon_{ij}(t) - \frac{1}{2}[u_{i,j}(t) + u_{j,i}(t)] = 0$$
 (13)

或率型几何方程: 
$$\dot{\varepsilon}_{ij}(t) - \frac{1}{2} [\dot{u}_{i,j}(t) + \dot{u}_{j,i}(t)] = 0$$
 (14)

其中 $\sigma_{ij}$ , $\varepsilon_{ij}$ , $u_i$ 及 $F_i$ 分别为应力,应变,位移及体力分量(i, j = 1,2,3)。本构方程可根据所讨论问题的具体情况,选用下面四组本构方程中的某一组<sup>[11, 12]</sup>

微分型本构方程: 
$$\begin{cases} 畸变方程: P_1(D)S_{ij} = Q_1(D)e_{ij} \\ \text{体变方程: } P_2(D)\sigma_{ii} = Q_2(D)\varepsilon_{ii} \end{cases}$$
(15)

曲于
$$\sigma_{ij} = S_{ij} + \frac{1}{3}\delta_{ij}\sigma_{ii}$$
、 $\varepsilon_{ij} = e_{ij} + \frac{1}{3}\delta_{ij}\varepsilon_{ii}$ ,所以可将(15)式合并写为  
 $\sigma_{ij} = \frac{Q_1(D)}{P_1(D)}e_{ij} + \frac{1}{3}\delta_{ij}\frac{Q_2(D)}{P_2(D)}\varepsilon_{ii}$ (或 $\varepsilon_{ij} = \frac{P_1(D)}{Q_1(D)}S_{ij} + \frac{1}{3}\delta_{ij}\frac{P_2(D)}{Q_2(D)}\sigma_{ii}$ ) (16)

其中  $P_i$ 、  $Q_i(i=1,2)$ 是微分算子  $D=\frac{d}{dt}$ 、  $D^2=\frac{d^2}{dt^2}$ 、 ......的多项式, 即

$$\begin{cases} P_1(D) = \sum_{k=0}^{n_1} a_k D^k , Q_1(D) = \sum_{k=0}^{m_1} b_k D^k \\ P_2(D) = \sum_{k=0}^{n_2} c_k D^k , Q_2(D) = \sum_{k=0}^{m_2} d_k D^k \end{cases}$$

 $S_{ii}, e_{ii}$  分别为应力,应变偏量;  $\sigma_{ii}, \varepsilon_{ii}$  分别为应力,应变张量的第一不变量;

$$\delta_{ij} = \begin{cases} 1 & \exists i = j 时 \\ 0 & \exists i \neq j \eta \end{cases}.$$

积分松弛型本构方程:

$$\begin{cases} 畸变方程: S_{ij}(t) = G_1 * de_{ij} \\ \phi 变方程: \sigma_{ii}(t) = G_2 * d\varepsilon_{ii} (当体积变化为弹性时可写为\sigma_{ii} = 3K\varepsilon_{ii}) \end{cases}$$
(17)

积分蠕变型本构方程:

81

其中\*表示"卷积",例如 $f * dg = \int_{-\infty}^{+\infty} f(t-s)dg(s); G_1, G_2 分别为切变和体变松弛模量;$   $J_1, J_2 分别为切变和体变蠕变柔量; K = \frac{E}{3(1-2\mu)}, E, \mu 分别为体积模量,弹性模量和$ Poisson 比。 定解条件为: 应力边界条件:  $\sigma_{ij}(t)n_j - \overline{P}_i(t) = 0$  在  $S_P \bot$  (19)

位移边界条件:  $u_i(t) - \overline{u}_i(t) = 0$  在  $S_u$ 上 (20)

或率型位移边界条件: $\dot{u}_i(t) - \dot{\overline{u}}_i(t) = 0$ 在 $S_u$ 上(21)

#### 2. 基于最小功耗原理的准静态粘弹性力学率型变分原理的两种基本形式:

根据最小功耗原理,在满足准静态粘弹性力学基本方程及定解条件的情况下应有

$$\begin{cases} \delta \dot{W}(t) = \delta \{ \iiint_{v} F_{i}(t) \dot{u}_{i}(t) dv + \iint_{S_{p}} \overline{P_{i}}(t) \dot{u}_{i}(t) ds \} = 0 \\ \delta [\dot{U}_{S}(t) + \dot{U}_{H}(t)] = \delta \{ \iiint_{v} \sigma_{ij}(t) \dot{\varepsilon}_{ij}(t) dv \} = 0 \end{cases}$$

$$(22)$$

在引入 Lagrange 乘子  $\mu_i$ 、  $\lambda_{ij} = \lambda_{ji}$ 、  $\lambda'_{ij} = \lambda'_{ji}$ 、  $\mu'_i$ 、  $\mu''_i$  (*i*, *j*=1, 2, 3)之后则有

$$\begin{cases} \delta\{\iiint_{v}F_{i}(t)\dot{u}_{i}(t)dv + \iint_{S_{p}}\overline{P}_{i}(t)\dot{u}_{i}(t)ds + \iiint_{v}\mu_{i}[\sigma_{ij,j}(t) + F_{i}(t)]dv + \iint_{v}\lambda_{ij}[\dot{\varepsilon}_{ij}(t) - \frac{1}{2}(\dot{u}_{i,j}(t) + \dot{u}_{j,i}(t))]dv \\ + \iint_{v}\lambda_{ij}'[\sigma_{ij}(t) - (\frac{Q_{1}(D)}{P_{1}(D)}e_{ij}(t) + \frac{1}{3}\delta_{ij}\frac{Q_{2}(D)}{P_{2}(D)}\varepsilon_{ii}(t))]dv + \iint_{S_{p}}\mu_{i}'[\sigma_{ij}(t)n_{j} - \overline{P}_{i}(t)]ds + \iint_{S_{u}}\mu_{i}''[\dot{u}_{i}(t) - \dot{\overline{u}}_{i}(t))ds \} = 0 \\ \delta\{\iint_{v}\sigma_{ij}(t)\dot{\varepsilon}_{ij}(t)dv + \iint_{v}\mu_{i}[\sigma_{ij,j}(t) + F_{i}(t)]dv + \iint_{v}\lambda_{ij}[\dot{\varepsilon}_{ij}(t) - \frac{1}{2}(\dot{u}_{i,j}(t) + \dot{u}_{j,i}(t))]dv \\ + \iint_{v}\lambda_{ij}'[\sigma_{ij}(t) - (\frac{Q_{1}(D)}{P_{1}(D)}e_{ij}(t) + \frac{1}{3}\delta_{ij}\frac{Q_{2}(D)}{P_{2}(D)}\varepsilon_{ii}(t))]dv + \iint_{S_{p}}\mu_{i}'[\sigma_{ij}(t)n_{j} - \overline{P}_{i}(t)]ds + \iint_{S_{u}}\mu_{i}''[\dot{u}_{i}(t) - \dot{\overline{u}}_{i}(t)ds \} = 0 \end{cases}$$

$$(23)$$

(22)或(23)式即为在准静态情况下基于最小功耗原理的粘弹性力学率型变分原理的条件或无条件变分表示式的两种基本形式。因为最小功耗原理是一个关于过程中任一时刻均成立的瞬态性率型原理,所以其中的物理方程采用了微分型,而几何方程及位移边界条件则采用了率型形式。以(22)或(23)式表示的原理的物理意义是:准静态情况下粘弹性力学问题的真实解答,必使过程中任意时刻的总外力功消耗率*啦*(*t*)(或与之相当的*Ü<sub>s</sub>*(*t*)+*Ü<sub>H</sub>(<i>t*))取最小值。

#### 五. 应用举例

例 1: 设如图所示三杆桁架是由 Maxwell 体制成,且当 *t*=0 时有 *P*(*t*)=*P*(0)=*P*<sub>0</sub>,与 *t* 时刻对应的荷载为 *P*(*t*),试按(23)之第一式求在任意时刻 *t* 时桁架各杆的应力、应变及 *D* 点的位移。

解:由于不计体力且各杆均处于均匀应力状态,故对本例而言平衡方程(12)式自然满足, 因为讨论的是一维问题,所以物理方程(15)式根据(8)式可写为 $\dot{\epsilon}_1(t) - [\frac{\dot{\sigma}_1(t)}{E} + \frac{\sigma_1(t)}{\eta}] = 0$ ,  $\dot{\epsilon}_2(t) - [\frac{\dot{\sigma}_2(t)}{E} + \frac{\sigma_2(t)}{\eta}] = 0$ (其中下标 1,2分别表示与杆①,②对应的相应物理量),应力边 界条件(19)式化为 $\sigma_1(t) + \sqrt{3}\sigma_2(t) - P(t) = 0$ 。几何方程(14)式及位移边界条件(21)式则化为  $\dot{\epsilon}_1(t) - \frac{\dot{u}_{yD}(t)}{h} = 0$ , $\dot{\epsilon}_2(t) - \frac{3\dot{u}_{yD}(t)}{4h} = 0$ ,其中 $\dot{u}_{yD}$ 为D点的沿垂直方向的位移。综上,(23)之 第一式对本问题可表为:

$$\delta\{P(t)\dot{u}_{yD}(t) + \lambda_{1}[\dot{\varepsilon}_{1}(t) - \frac{\dot{u}_{yD}(t)}{h}] + \lambda_{2}[\dot{\varepsilon}_{2}(t) - \frac{3\dot{u}_{yD}(t)}{4h}] + \lambda_{1}'[\dot{\varepsilon}_{1}(t) - (\frac{\dot{\sigma}_{1}(t)}{E} + \frac{\sigma_{1}(t)}{\eta})] + \lambda_{2}'[\dot{\varepsilon}_{2}(t) - (\frac{\dot{\sigma}_{2}(t)}{E} + \frac{\sigma_{2}(t)}{\eta})] + \mu'[\sigma_{1}(t) + \sqrt{3}\sigma_{2}(t) - P(t)]\} = 0$$
(24)

因为本问题属于给定荷载情况下的准静态问题,所以应力与荷载持续时间无关,而只与加载 过程有关,如此 $\dot{\sigma}_1(t)$ 、 $\dot{\sigma}_2(t)$ 均可视为常数(即可设  $P(t)=P_0+Kt)$ ,故 $\dot{\sigma}_1(t)$ 、 $\dot{\sigma}_2(t)$ 不参加变 分,所以由(24)式有:

$$\begin{cases} \mu' - \frac{\lambda_1'}{\eta} = 0 ; \sqrt{3}\mu' - \frac{\lambda_2'}{\eta} = 0 ; \dot{\varepsilon}_1(t) - \frac{\dot{u}_{yD}(t)}{h} = 0 ; \dot{\varepsilon}_2(t) - \frac{3\dot{u}_{yD}(t)}{4h} = 0; \\ \dot{\varepsilon}_1(t) - [\frac{\dot{\sigma}_1(t)}{E} + \frac{\sigma_1(t)}{\eta}] = 0; \dot{\varepsilon}_2(t) - [\frac{\dot{\sigma}_2(t)}{E} + \frac{\sigma_2(t)}{\eta}] = 0; \\ \sigma_1(t) + \sqrt{3}\sigma_2(t) - P(t) = 0; \\ \lambda_1 + \lambda_1' = 0 ; \lambda_2 + \lambda_2' = 0 ; P(t) - \frac{\lambda_1}{h} - \frac{3\lambda_2}{4h} = 0 \end{cases}$$
(25)

(25)式共有 10 个方程,而待定的未知量包括 Lagrange 乘子在内也是 10 个,因此由(25)式可 求得问题的解答。但由于联立求解 10 个方程过于麻烦,在实际求解时可按如下方式进行: 由(25)之 3、4、5、6 式可见有  $\varepsilon_2(t) = \frac{3}{4} \varepsilon_1(t) \ \sigma_2(t) = \frac{3}{4} \sigma_1(t)$ ,于是将  $\dot{\varepsilon}_1(t) = \frac{\dot{u}_{yD}(t)}{h}$ 代入(24) 式并注意到上述的  $\varepsilon_1(t) \ \sigma_1(t) \ \varepsilon_2(t) \ \sigma_2(t)$ 之间的关系,即可得

$$\delta\{P(t)\dot{u}_{yD}(t) + \lambda_{1}'[\frac{\dot{u}_{yD}(t)}{h} - (\frac{\dot{\sigma}_{1}(t)}{E} + \frac{\sigma_{1}(t)}{\eta})] + \lambda_{2}'\frac{3}{4}[\frac{\dot{u}_{yD}(t)}{h} - (\frac{\dot{\sigma}_{1}(t)}{E} + \frac{\sigma_{1}(t)}{\eta})]$$

+ 
$$\mu'[\sigma_1(t) + \frac{3\sqrt{3}}{4}\sigma_1(t) - P(t)]\} = 0$$

再将由(25)第3、5两式得到的 $\dot{u}_{yD}(t) = h[\frac{\dot{\sigma}_1(t)}{E} + \frac{\sigma_1(t)}{\eta}]$ 代入上式,于是(24)式即可简化为

$$\delta\{P(t)h[\frac{\dot{\sigma}_1(t)}{E} + \frac{\sigma_1(t)}{\eta}] + \mu'[\sigma_1(t) + \frac{3\sqrt{3}}{4}\sigma_1(t) - P(t)]\} = \delta\{\varphi[\sigma_1(t), \mu']\} = 0$$
(7.57)'

因 为 
$$\dot{u}_{yD}(t) = h\dot{\varepsilon}_{1}(t)$$
, 所 以 有  $u_{yD}(t) = u_{yD}(0)$   
+ $h[\varepsilon_{1}(t) - \varepsilon_{1}(0)] = u_{yD}(0) + \frac{4h}{4+3\sqrt{3}} [\frac{1}{E} \int_{0}^{t} \dot{P}(t)dt + \frac{1}{\eta} \int_{0}^{t} P(t)dt]$ , 其中 $u_{yD}(0) = h\varepsilon_{1}(0) = \frac{h}{E} \cdot \frac{4P_{0}}{4+3\sqrt{3}} \circ$   
当  $P(t) = P_{0} = 常 数 时$ , 则 有  $\varepsilon_{1}(t) = \frac{4P_{0}}{4+3\sqrt{3}} (\frac{1}{E} + \frac{t}{\eta})$ ;  $\varepsilon_{2}(t) = \frac{3P_{0}}{4+3\sqrt{3}} (\frac{1}{E} + \frac{t}{\eta})$ ;  
 $u_{yD}(t) = \frac{4hP_{0}}{4+3\sqrt{3}} (\frac{1}{E} + \frac{t}{\eta})$ ,  $\sigma_{1} = \frac{4}{4+3\sqrt{3}} P_{0}$ ;  $\sigma_{2} = \frac{3}{4+3\sqrt{3}} P_{0}$  o 另外将前面求得的

$$\mu' = -\frac{4}{4+3\sqrt{3}} \frac{h}{\eta} P(t) 代 \lambda(25) 之 第 1 式 可得 \lambda'_1 = \eta \mu' = -\frac{4}{4+3\sqrt{3}} hP(t) \circ \text{ 由}(25) 之 第 8 式 可得$$

$$\lambda_1 = -\lambda_1' = \frac{4}{4+3\sqrt{3}}hP(t) \circ \pm (25)$$
之第 2 式有  $\lambda_2' = \sqrt{3}\eta\mu' = -\frac{4\sqrt{3}}{4+3\sqrt{3}}hP(t) \circ B \pm (25)$ 之第 9 式

又有 $\lambda_2 = -\lambda'_2 = \frac{4\sqrt{3}}{4+3\sqrt{3}}hP(t)$ 。可以验证,以上应力,应变及 D 点的位移与按弹性力学现有

方法求得的结果完全一样。

例 2: 按(23)之第 2 式求解上例。

解:对上例而言,(23)之第2式可表为:

$$\delta\{h\sigma_{1}(t)\dot{\varepsilon}_{1}(t) + \frac{4h}{\sqrt{3}}\sigma_{2}(t)\dot{\varepsilon}_{2}(t) + \lambda_{1}[\dot{\varepsilon}_{1}(t) - \frac{\dot{u}_{yD}(t)}{h}] + \lambda_{2}[\dot{\varepsilon}_{2}(t) - \frac{3\dot{u}_{yD}(t)}{4h}] + \lambda_{1}'[\dot{\varepsilon}_{1}(t) - (\frac{\dot{\sigma}_{1}(t)}{E} + \frac{\sigma_{1}(t)}{\eta})] + \lambda_{2}'[\dot{\varepsilon}_{2}(t) - (\frac{\dot{\sigma}_{2}(t)}{E} + \frac{\sigma_{2}(t)}{\eta})] + \mu'[\sigma_{1}(t) + \sqrt{3}\sigma_{2}(t) - P(t)]\} = 0$$
(26)

由(26)式有

$$\begin{cases} h\dot{\varepsilon}_{1}(t) - \frac{\lambda_{1}'}{\eta} + \mu' = 0; \frac{4h}{\sqrt{3}}\dot{\varepsilon}_{2}(t) - \frac{\lambda_{2}'}{\eta} + \sqrt{3}\mu' = 0; \dot{\varepsilon}_{1}(t) - \frac{\dot{u}_{yD}(t)}{h} = 0; \dot{\varepsilon}_{2}(t) - \frac{3\dot{u}_{yD}(t)}{4h} = 0; \\ \dot{\varepsilon}_{1}(t) - [\frac{\dot{\sigma}_{1}(t)}{E} + \frac{\sigma_{1}(t)}{\eta}] = 0; \dot{\varepsilon}_{2}(t) - [\frac{\dot{\sigma}_{2}(t)}{E} + \frac{\sigma_{2}(t)}{\eta}] = 0; \sigma_{1}(t) + \sqrt{3}\sigma_{2}(t) - P(t) = 0; \\ h\sigma_{1}(t) + \lambda_{1} + \lambda_{1}' = 0; \frac{4h}{\sqrt{3}}\sigma_{2}(t) + \lambda_{2} + \lambda_{2}' = 0; \lambda_{1} + \frac{3\lambda_{2}}{4} = 0 \end{cases}$$
(27)

(27)式共有 10 个方程,而待定的未知量包括 Lagrange 乘子在内也是 10 个,因此由(27)式可  
求得问题的解答。与上例类似,本例也可按如下简捷方式求解:将(27)之 3、4 两式即  
$$\dot{\varepsilon}_1(t) = \frac{\dot{u}_{yD}(t)}{h} 和 \dot{\varepsilon}_2(t) = \frac{3\dot{u}_{yD}(t)}{4h} 代入(26)式可得$$
  
 $\delta\{\sigma_1(t)\dot{u}_{yD}(t) + \sqrt{3}\sigma_2(t)\dot{u}_{yD}(t) + \lambda'_1[\frac{\dot{u}_{yD}(t)}{h} - (\frac{\dot{\sigma}_1(t)}{E} + \frac{\sigma_1(t)}{\eta})] + \lambda'_2[\frac{3}{4}\frac{\dot{u}_{yD}(t)}{h} - (\frac{\dot{\sigma}_2(t)}{E} + \frac{\sigma_2(t)}{\eta})]$   
 $+ \mu'[\sigma_1(t) + \sqrt{3}\sigma_2(t) - P(t)]\} = 0$  (26)'

再将由(27)之 3、5 两式得到的 $\frac{\dot{u}_{yD}(t)}{h} = \frac{\dot{\sigma}_1(t)}{E} + \frac{\sigma_1(t)}{\eta}$ 代入(26)'式,并注意到 $\sigma_2(t) = \frac{3}{4}\sigma_1(t)$ ,则可得到

$$\delta\{\sigma_{1}(t)h[\frac{\dot{\sigma}_{1}(t)}{E} + \frac{\sigma_{1}(t)}{\eta}] + \frac{3\sqrt{3}}{4}h\sigma_{1}(t)[\frac{\dot{\sigma}_{1}(t)}{E} + \frac{\sigma_{1}(t)}{\eta}] + \mu'[\sigma_{1}(t) + \frac{3\sqrt{3}}{4}\sigma_{1}(t) - P(t)]\}$$
$$= \delta\{\frac{4+3\sqrt{3}}{4}\sigma_{1}(t)h[\frac{\dot{\sigma}_{1}(t)}{E} + \frac{\sigma_{1}(t)}{\eta}] + \mu'[\frac{4+3\sqrt{3}}{4}\sigma_{1}(t) - P(t)]\} = 0 \qquad (26)''$$

由(26)"式有
$$\frac{4+3\sqrt{3}}{4}\sigma_1(t) - P(t) = 0$$
;  $h[\frac{\dot{\sigma}_1(t)}{E} + \frac{2\sigma_1(t)}{\eta}] + \mu' = 0$ 。于是有\_\_\_\_\_及

$$\mu' = -\frac{4h}{4+3\sqrt{3}} \quad [\frac{\dot{P}(t)}{E} + \frac{2P(t)}{\eta}] \ \mathcal{B} \ \dot{\varepsilon}_1(t) = \frac{4}{4+3\sqrt{3}} [\frac{\dot{P}(t)}{E} + \frac{P(t)}{\eta}] \ \mathcal{K} \ \lambda \ (27) \ \dot{\mathcal{L}} \ \ddot{\mathfrak{R}} \ 1 \ \vec{\mathfrak{K}} \ \vec{\mathfrak{T}} \ \vec{\mathfrak{R}}$$

$$\lambda_1' = -\frac{4}{4+3\sqrt{3}}hP(t), 类似地由(27)之第2,8,9 三式可求得\lambda_2' = -\frac{4\sqrt{3}}{4+3\sqrt{3}}hP(t) \partial_t \lambda_1 = \lambda_2 = 0.$$

以上两例表明,由基于最小功耗原理的准静态粘弹性力学率型变分原理的两种基本形式,都可以求得问题的正确解答。这是因为满足(23)中的任何一式,实际上就意味着满足准静态粘弹性力学问题的全部基本方程及定解条件。但当采用(23)之第1式或第2式时,其结果中的Lagrange乘子的物理意义将会是不一样的。

#### 六. 结束语

文献 [7] 正式出版后,受到一些专家,学者和有关专业研究生的关注,他们有的将该 文献提出的解决问题的新思路和新方法,用于所研究的题目,所获成果散见于发表在包括"中 国科学","电波科学学报","科学创新导报","岩土力学","建筑结构学报","岩石力学与 工程学报","固体力学学报","材料科学与工程学报"等权威刊物在内的一系列学术论文之 中;有的则在一些高校的自然科学学报上撰写专文,对有关问题与作者进行深入讨论。但专 门研究最小耗能原理在流变固体力学中应用的文章还很少见到。本文表明:最小耗能原理在 流变固体力学领域也可发挥重要作用。

#### 参考文献

[1] Finlayson, Bruch A., The Method of Weighted Residuals and Variational Principles, Academic Press, Inc. 1972

- [2] I. Prigogine, Acad. Roy. Bely., Bull. Classe Sci., 31, 600(1945)
- [3] Yang C.T. Theory of Minimum Energy and Energy Dissipation Rate, Encyclopedia of Fluid Mechanics, Gulf Publishing Company, 1986.
- [4] 杨志达。力,能量,熵和能耗率。泥沙情报。1992(1)
- [5] 徐国宾, 陈继建。流体最小熵产生原理与最小能耗率原理(I), 水利学报: 2003 (5).
- [6] 徐国宾, 陈继建。流体最小熵产生原理与最小能耗率原理(II), 水利学报: 2003(6).
- [7] 周筑宝,最小耗能原理及其应用,北京:科学出版社,2001
- [8] 周筑宝, 唐松花.功耗率最小与工程力学中的各类变分原理, 北京: 科学出版社, 2007
- [9] 杨绪灿,杨桂通,徐秉业. 粘塑性力学概论. 中国铁道出版社,1985.
- [10] 袁龙蔚,流变力学,北京:科学出版社 1986
- [11] 张淳源, 粘弹性断裂力学, 武汉: 华中理工大学出版社 1994
- [12] R.M.克里斯坦森著,郝松林等译,粘弹性力学引论,北京:科学出版社,1990

## $SSBR/SiO_2$ 混炼胶的动态粘弹行为<sup>\*</sup>

宋义虎\*\*,孙 晋,郑 强 (高分子合成与功能构造教育部重点实验室 浙江大学高分子科学与工程学系 杭州 310027)

摘要:研究了白炭黑(SiO<sub>2</sub>)填充溶液聚合丁苯橡胶(SSBR)的动态流变行为,考察了时间-浓度叠加 (Time-concentration superposition, TCS)原理在粒子填充橡胶中的应用,获得以未填充 SSBR 为基准的流变叠 加曲线。流变叠加曲线在低频下呈现模量平台,复数黏度呈现剪切变稀行为,而损耗因子 tan*δ*在特定频率 下出现峰值。基于刚性粒子所导致的应变放大效应以及 SiO<sub>2</sub>粒子间 SSBR 分子的受限运动,探讨了 TCS 模量平移因子  $A_{\rm G}$ 与频率平移因子  $A_{\rm o}$ 随 SiO<sub>2</sub>体积分数φ的变化。 $A_{\rm G}$ 与 $A_{\rm o}$ 均为 $\phi$ 的标度函数,但  $A_{\rm G}\sim \phi$ 关系不 符合粒子聚集体团聚(cluster-cluster aggregation, CCA)模型。讨论了偶联剂 3-辛酰基硫代-1-丙基三乙氧基硅 烷(NXT)对动态流变行为的影响。NXT 不影响性叠加曲线的低频平台模量与剪切变稀幂律指数。然而,与 不含偶联剂的混炼胶相比,NXT 造成 SSBR 特征松弛时间缩短,稠度与 $A_{\rm G}$ 增大。

关键词:溶聚丁苯橡胶,白炭黑,动态粘弹性,时间-浓度叠加(Time-concentration superposition, TCS)原理, 应变**放大效应** 

粒子填充是橡胶补强的的主要途径。在仅考虑粒子几何效应的情况下,可用Einstein方 程及其修正形式描述橡胶补强机理<sup>[1]</sup>。在高含量下,炭黑、白炭黑等活性粒子团聚,并进一 步形成粒子网路,补强效果取决于粒子聚集体的团聚(cluster-cluster aggregation, CCA)过程 <sup>[2]</sup>。然而,不管是Einstein方程还是CCA模型,均忽略高分子链对填料粒子的拓扑屏蔽效应<sup>[3]</sup>。 粒子填充导致结合橡胶与玻璃化转变温度(*T*g)升高的界面层的形成<sup>[4]</sup>,使弹性有效链段分子 量及分子能动性降低<sup>[5]</sup>。刚性粒子的存在造成显著的应变放大效应,即粒子间隙中橡胶基体 的局部应变远大于宏观应变<sup>[6]</sup>。现有橡胶补强模型均不涉及分子能动性变化与应变放大效 应。

沉淀法白炭黑(SiO<sub>2</sub>)填充溶液聚合丁苯橡胶(SSBR)可应用于低滚动阻力、低油耗"绿色 轮胎"胎面胶。为改善亲水性SiO<sub>2</sub>在橡胶中的分散性,提高橡胶加工性,通常在混炼胶中添 加硫硅烷偶联剂。本文以SSBR/SiO<sub>2</sub>混炼胶为模型,从分子能动性与应变放大效应角度分析 填充橡胶的线性粘弹性,探讨橡胶补强机理,并考察偶联剂对补强效果的影响。

#### 1 实验部分

#### 1.1 原材料

溶液聚合丁苯橡胶(SSBR, PR1205, 苯乙烯含量 25 %, 顺式-1,4-结构含量 35 %), 奇美 实业股份有限公司; 沉淀法白炭黑(SiO<sub>2</sub>, Ultrasil VN3 GR, pH 5.4~7.0, 比表面积 175 m<sup>2</sup>/g), 德国 DEGUSSA 公司; 3-辛酰基硫代-1-丙基三乙氧基硅烷(NXT), 美国 Crompton 公司; 硬 脂酸、石蜡、氧化锌、N-(1,3-二甲基丁基)-N'苯基对苯二胺(6PPD), 上海景惠化工有限公司。

#### 1.2 样品的制备

混炼胶组成(phr)为: SSBR 100; SiO<sub>2</sub> 0~50; NXT 偶联剂 0 或 7; 氧化锌 2.5; 硬脂酸

<sup>\*</sup>纪念杨士林先生诞辰90周年; \*\*通讯联系人, Email:<u>s yh0411@zju.edu.cn</u>

1.0; 石蜡 1.5; 6PPD 2.0。采用开炼机在 50 °C 初混 SSBR、SiO<sub>2</sub> 与其它助剂, 随后采用 Haake 流变仪在 150 °C 混炼 10 min, 将混炼胶于 150 °C、10 MPa 下压成直径 25 mm、厚度 1.5 mm 的样品。

#### 1.3 测试

透射电子显微镜(TEM),用 TEM 分析仪(JEM-1230, Electron Co., 日本)观察未填充 SSBR 低温超薄切片(厚度 200~300 nm)形态。动态力学分析(DMA),采用单悬臂模式在 TA Q800 DMA (TA Instruments, USA)上进行测试,频率为 1 Hz,升温速率为 3 °C min<sup>-1</sup>。动态 流变,采用平行板模式在先进流变扩展系统(ARES, TA Instrument,美国)上进行频率扫描测 试,温度为 150 °C,应变为 0.1 %。

#### 2 结果与讨论

#### 2.1 SSBR 的微观相分离与玻璃化转变

图1给出SSBR的TEM显微形貌。SSBR呈现微观相分离,形成宽约10 nm的相互连接的 片层结构。图2给出SSBR的DMA曲线。储能模量(*E*)随温度(*T*)升高而降低,SSBR依次经历 玻璃态、玻璃化转变与橡胶平台区。由tan*d*曲线可见,SSBR的玻璃化转变温度(*T*g)为-63 °C。 在橡胶平台区,SSBR在85 °C出现次级转变,对应聚苯乙烯微区的玻璃化转变。TEM与DMA 分析表明,SSBR分子含有聚苯乙烯短嵌段,形成片层结构,分散于无规SBR橡胶基体中。



Fig. 1 TEM micrograph of unfilled SSBR



Fig. 2 Temperature dependences of storage modulus E' and loss tangent tan $\delta$  at frequency 1 Hz for unfilled SSBR



Fig. 3 Storage modulus G' (solid symbol), loss modulus G'' (hollow symbol) and loss tangent tan $\delta$  as a function of

frequency  $\omega$  for the SSBR/silica compounds containing 7 phr NXT coupling agent

#### 2.2 SSBR/SiO2混炼胶的流变特性

图3给出SiO<sub>2</sub>体积分数( $\varphi$ )对含7 phr NXT偶联剂的SSBR/SiO<sub>2</sub>混炼胶动态流变行为的影响。在给定频率( $\omega$ )下,混炼胶动态储能模量(G')与损耗模量(G')均随 $\varphi$ 增大而显著增大,同时tan $\delta$ 值显著降低。 $\varphi$ =0时,低频区( $\omega$  < 2 rad s<sup>-1</sup>) G'>G'',且G'的频率依赖性较弱;在高频区( $\omega$  > 2 rad s<sup>-1</sup>),G'与G''极为接近。在测试 $\omega$ 范围内,未填充SSBR由于微观相分离而呈现平台区-转变区的流变特性<sup>[7]</sup>,其tan $\delta$ 峰值频率 $\omega_p$ 对应平台区向转变区过渡的特征时间 $\tau$ 。随 $\varphi$ 增大,G'与G''的频率依赖性逐渐减弱。 $\varphi$ =0.20时,G'与G''在 $\omega$ <0.1 rad s<sup>-1</sup>几乎与 $\omega$ 无关,呈现粒子填充体系典型的低频平台特征<sup>[4]</sup>。通常认为,该类固行为与三维粒子网络的形成有关。 $\omega_p$ 随 $\varphi$ 增大而向高频移动,与SiO<sub>2</sub>粒子吸附SSBR分子链并约束其运动相矛盾。不含NXT偶联剂时,混炼胶呈现与图3类似的流变行为,只是相同SiO<sub>2</sub>含量下低频模量增加更为显著。

#### 2.3 混炼胶流变特性的标度讨论

Coussot<sup>[8]</sup>考察了水性粘土悬浮液的稳态流变行为,采用约化剪切应力τ/τ<sub>c</sub>~约化应变速 率 $\eta\dot{\gamma}/\tau_c$ 图来归一化悬浮液的流动曲线。这里, $\tau$ 与 $\dot{\gamma}$ 分别为剪切应力与应变速率, $\tau_c$ 为屈 服应力, $\eta$ 为稳态黏度。Trappe与Weitz<sup>[9]</sup>发现,将油性炭黑悬浮液的动态流变数据分别沿模 量轴、频率轴平移,可获得不同炭黑含量情况下的叠加曲线。这些研究揭示了粒子悬浮液的 时间-浓度叠加(Time-concentration superposition, TCS)原理。TCS原理被成功地应用于 Laponite层柱粘土/8%聚氧乙烯悬浮液<sup>[10]</sup>、多壁纳米炭管/低分子量聚异丁烯悬浮液<sup>[11]</sup>、单壁 纳米炭管/聚氧乙烯复合材料<sup>[12]</sup>与炭黑/聚乙烯复合材料<sup>[13]</sup>的动态流变行为。应用TCS原理 时,经验上分别将纵向、横向平移因子取静态屈服模量 $G_c$ 与 $\eta/G_c$ 。Mongruel与Cartault<sup>[14]</sup> 发现,炭黑或SiO<sub>2</sub>填充丁苯橡胶的高频( $\omega$ > 20 rad s<sup>-1</sup>)模量曲线与未填充胶平行,而tan $\delta$ 曲线 与未填充胶重合,提出采用高频G比值来定义补强因子。Gleissle与Hochstein<sup>[15]</sup>发现,玻璃 珠、石英粉、石灰石粉等悬浮液的复数模量 $G^*$ 曲线平行于硅油悬浮剂,采用悬浮液与悬浮 剂 $G^*$ 比即可简单定义应变放大因子。可见,目前对TCS平移因子缺乏统一的定义。SSBR/SiO<sub>2</sub> 混炼胶的动态流变行为明显不同于丁苯橡胶混炼胶及玻璃珠等悬浮液。在所研究 $\omega$ 范围内, SSBR/SiO<sub>2</sub>混炼胶模量曲线不平行,tan $\delta$ 曲线不重合,也无法确定稳态黏度。因而,难以采 用文献建议的方法确定平移因子。

在动态剪切应变 $\gamma^* = \gamma_0 e^{i\omega t}$ 作用下,粒子填充体系承受宏观应力 $\sigma^* = \sigma_0 e^{i(\omega t+\delta)}$ ,应变速 率为 $\dot{\gamma}^* = i\omega\gamma^*$ ,复数模量与复数黏度分别为 $G^* = \sigma^* / \gamma^* 与 \eta^* = \sigma^* / \dot{\gamma}^*$ 。这里, $\gamma_0$ 、 $\sigma_0$ 分别为 宏观应变幅度与应力幅度, $\delta$ 为相位角。微观上,粒子间橡胶基体的局部应变 $\gamma_{Loc}^*$ 远大于宏 观应变 $\gamma^{*[6]}$ ,二者间关系记为 $\gamma_{Loc}^* = A_G\gamma^*$ ,其中 $A_G > 1$ 为应变放大因子。粒子间橡胶基体的 复数模量为 $G_{Loc}^* = \sigma^* / \gamma_{Loc}^* = \sigma^* / (A_G\gamma^*) = G^* / A_G$ ,复数黏度为 $\eta_{Loc}^* = \eta^* / A_G$ 。可见,与粒子 间橡胶基体的局部性质相比,粒子填充导致橡胶宏观模量与黏度均增大 $A_G$ 倍。另一方面, 刚性粒子约束粒子间橡胶分子运动,分子松弛时间延长。在双对数坐标上,将填充橡胶的流 变曲线沿模量轴平移log( $A_G^{-1}$ )个单位、沿频率轴平移log $A_{\omega}(A_{\omega} < 1)$ 个单位,可与未填充橡胶 的流变曲线叠合。 图4给出不同 $\phi$ 下SSBR/SiO<sub>2</sub>混炼胶的动态流变叠加曲线。为考察偶联剂的影响,将不含 偶联剂与含7 phr NXT偶联剂的数据绘制于同一图,其中将不含偶联剂的数据沿模量轴上移1 个数量级。由图4可见,经曲线平移后,填充橡胶的流变学参数 $G'、G''、|G^*|、|\eta^*|、tan \delta$ 基本 与未填充橡胶数据重合。叠加曲线显示, $G'、G''与|G^*|$ 在低频区呈现与 $\omega$ 无关的平台值。这 表明,由于粒子的拓扑限制以及粒子对SSBR分子链的吸附,粒子间受限橡胶在长时区不会 发生终端流动。

由图4(b)可见,  $|\eta^*|$ 随*ω*增加而显著降低,呈现剪切变稀。采用 $|G^*|=|G_0^*|+K\omega^{n}|^{13}$ 与  $|\eta^*|=|G^*|/\omega=|G_0^*|/\omega+K\omega^{n-1}$ 分别拟合 $|G^*|\sim\omega$ 与 $|\eta^*|\sim\omega$ 叠加曲线数据,可得到低频平台模量  $|G_0^*|$ 、稠度*K*与幂律指数*n* (*n* < 1)。图4(b)中实线与虚线分别显示 $|G^*|$ 与 $|\eta^*|$ 的拟合结果。根 据曲线拟合,不含偶联剂与含7 phr NXT偶联剂的混炼胶的 $|G_0^*|$ 分别为2.8 kPa与2.2 kPa,*K* 分别为9.4 kPa s<sup>n</sup>与4.4 kPa s<sup>n</sup>,*n*均为0.62。可见,偶联剂造成*K*显著降低,但不影响 $|G_0^*|$ 与*n*。



**Fig. 4** Master curves of *G*' (solid symbol), *G*" (hollow symbol), *G*\* (solid symbol),  $\eta^*$  (hollow symbol) and tan $\delta$  as a function of  $\omega$  for SSBR/SiO<sub>2</sub> compounds and influence of NXT on characteristic relaxation time as a function of  $\varphi$ 

The data for compounds containing 7 phr NXT are vertically shifted by one order of magnitude upward for clarity

由图4(a)与图4(c)可见, G"与tand随*w*增加而逐渐偏离叠加曲线,且*q*越大,偏离叠加曲 线的*w*值越低。这说明, SiO<sub>2</sub>粒子吸附SSBR链段,约束链段以及更小单元的运动,从而影 响高分子的高频(短时)松弛行为。根据tand叠加曲线的峰值频率*w*<sub>p</sub>可确定受限橡胶的特征松 弛时间*t*,如图4(d)所示。*t*随*q*增大而增大,而含NXT混炼胶的*t*低于不含偶联剂的混炼胶。 可见,偶联剂可降低SiO<sub>2</sub>粒子对SSBR分子运动的束缚。

图5显示平移因子与ø的关系。频率平移因子A。反比于τ,随ø增大而降低。应变放大因 子 $A_{G}$ 等价于橡胶补强因子,随 $\phi$ 增大而增大。不含偶联剂时, $A_{G}$ 明显大于含NXT的混炼胶。 CCA模型假设填料粒子在其平衡位置附近波动,其关联长度与橡胶缠结链段尺寸相当。 $\varphi$ 高 于临界值时,CCA模型预测剪切模量 $G \sim \varphi^{x}$ <sup>[2]</sup>,标度指数 $x = (3 + d_{\rm fB})/(3 - d_{\rm f}) = 3.5, d_{\rm f} = 1.8$ 与  $d_{\rm fB} = 1.3$ 分别为粒子聚集体及聚集体骨架的分维度。若不考虑填料粒子波动,则x = 5/(3- $d_{\rm f}$ ) =  $4.2^{[3]}$ 。采用  $A_{G} \sim \varphi^{x}$  拟合图5中的 $A_{G}$ 数据,发现不含偶联剂时 $x = 2.65 \pm 0.02$ ,而含7 phr NXT 时x=2.22±0.36,均明显低于CCA模型预测值,说明CCA模型并不适用于SiO<sub>2</sub>/SSBR体系。 虽有报导SiO2悬浮液<sup>[16,17]</sup>与SiO2填充硅橡胶<sup>[18]</sup>、聚丁二烯<sup>[4]</sup>及EVA共聚物<sup>[3]</sup>等体系符合CCA 模型,但也有例外体系,如SiO2填充聚异戊二烯(x=5.2)<sup>[19]</sup>、SiO2/聚氧乙烯溶液分散液(SiO2 含量较低时x = 3.3, SiO<sub>2</sub>含量较高时x=26.5)<sup>[20]</sup>。对于SiO<sub>2</sub>填充硅橡胶, x与SiO<sub>2</sub>粒子表面性 质有关<sup>[21]</sup>。对于亲水性SiO2粒子, x=7.2; 对于疏水改性的SiO2粒子, x=2.8; x随表面疏水性 提高而降低,与本文结果一致。可见,,忽略高分子或悬浮剂黏弹特性的CCA模型在描述 粒子填充体系的补强机理上具有局限性。Vermant<sup>[22]</sup>等人为,粒子填充高分子的低频流变数 据反映粒子渗流网络结构,而高频流变数据反映高分子运动,因而提出分别采用CCA模型 与Krieger-Dougherty方程来描述低频与高频下的G~o关系。然而,Krieger-Dougherty方程、 Einstein方程等经验方程通常用于悬浮液或填充体系的稳态黏度。事实上,SSBR/SiO2混炼胶 的动态流变行为与粒子间橡胶基体的松弛密切相关,流变叠加曲线主要反映SSBR分子链在 粒子间隙内的受限运动。由图5可见, $A_{\omega} \sim \phi$ 关系满足标度律 $A_{\omega} \sim \phi^{-\nu}$ ,最小二乘拟合给出y =4.00 ± 1.00 (不含偶联剂)与v = 1.54 ± 0.53 (含偶联剂)。文献报道<sup>[9]</sup>,粒子悬浮液或填充体系 TCS平移因子间存在标度关系,即 $A_{G} \sim A_{0}^{z}$ 。对于SSBR/SiO<sub>2</sub>混炼胶,应变放大效应与SSBR 分子松弛相互关联, z = -x/y。由图5, 不含偶联剂时, z = 0.66; 含7 phr NXT时, z = 1.44。



Fig. 5 Shift factors  $A_{\rm G}$  and  $A_{\omega}$  as a function of  $\varphi$  for SSBR/SiO<sub>2</sub> compounds with and without 7 phr NXT

综上所述,(1) TCS原理可应用于SSBR/SiO<sub>2</sub>混炼胶的动态流变行为,获得以未填充SSBR 为基准的流变叠加曲线;(2) 粒子填充造成橡胶基体的应变放大效应,并延迟橡胶分子松弛, 从而引入TCS模量平移因子A<sub>G</sub>与频率平移因子A<sub>o</sub>;(3) 基于填料粒子空间堆积的CCA模型不 能解释A<sub>G</sub>~*φ*关系,流变叠加曲线反映SSBR分子链在粒子间隙内的受限运动;(4) 在应用TCS 时,不需引入"粒子网络"、"渗流"、"结合橡胶"等观念,易于推广至其它粒子填充高分子体 系。由于SSBR呈现微观相分离,在所研究*o*范围内其流变行为处于平台区-转变区,因而尚 不能揭示SSBR受限松弛与本体松弛的本质区别。后续研究可采用时-温叠加原理获得SSBR 的终端流动曲线,或以其它均相橡胶基体为研究对象,着重考察TCS原理在终端区的应用, 以揭示橡胶受限运动对终端流动区黏弹特性的影响。

#### REFERENCES

- 1 Ahmed A, Jones FR. J Mater Sci ,1990 ,25 :4933 ~ 4942
- 2 Kluppel M, Adv Polym Sci, 2003, 164:1 ~ 86
- 3 Cassagnau P, Polymer, 2003, 44:2455 ~ 2462
- 4 Zhu ZY ,Thompson T ,Wang SQ ,von Meerwall ED ,Halasa A Macromolecules ,2005 ,38 :8816 ~ 8824
- 5 Luo H, Kluppel M, Schneider H. Macromolecules ,2004 ,37 :8000 ~ 8009
- 6 Rault J, Marchal J, Judeinstein P, Albouy PA. Macromolecules ,2006, 39:8356 ~ 8368
- 7 Ferry JD. Viscoelastic Properties of Polymers. New York : Wiley ,1980 ,56 ~ 59
- 8 Coussot P .Phys Rev Lett ,1995 ,74 :3971 ~ 3974
- 9 Trappe V, Weitz DA. Phys Rev Lett ,2000 ,85 :449 ~ 452
- 10 Daga VK ,Wagner NJ .Rheol Acta ,2006 ,45 :813 ~ 824
- 11 Hobbie EK ,Fry DJJ .Chem Phys ,2007 ,126 : 124907-1 ~ 7
- 12 Chatterjee T ,Krishnamoorti R .Phys Rev E ,2007 ,75: 050403-1 ~ 4
- 13 Jager KM , Eggen SS , Polymer , 2004 , 45 : 7681-7692
- 14 Mongruel A ,Cartault M .J Rheol ,2006 ,50 :115-135
- 15 Gleissle W ,Hochstein B .J Rheol ,2003 ,47 :897-910
- 16 Yziquel F, Carreau PJ. Tanguy PA. Rheol Acta, 1999, 38:14-25
- 17 Khan SA .Zoeller NJ .J Rheol ,1993 ,37 :1225-1235
- 18 Piau JM ,Dorget M ,Palierne JF .J Rheol ,1999 ,43 :305-314
- 19 Gurovich D , Macosko CW, Tirrell M .Rubber Chem Technol ,2004 ,76 :1-12
- 20 Ponton A, Quemada D, Lafuma F, Neel O. Colloid Surface A, 1996, 119 :255-259
- 21 Paquien J-N ,Galy J ,Gerard J-F ,Pouchelon A. Colloid Surfaces A: Physicochem. Eng. Aspects , 2005 ,260: 165 ~ 172
- 22 Vermant J ,Ceccia S ,Dolgovskij MK ,Maffettone PL ,Macosko CW .J Rheol ,2007 ,51 :429-450

#### DYNAMIC RHEOLOGICAL BEHAVIOR OF SSBR/SIO<sub>2</sub> COMPOUNDS

SONG Yihu<sup>\*</sup>, SUN Jin, ZHENG Qiang

(Key Laboratory of Macromolecular Synthesis and Functionalization, Ministry of Education , Department of Polymer Science and Engineering , Zhejiang University , Hangzhou 310027 China)

**Abstract** Dynamic rheological behaviors of silica (SiO<sub>2</sub>) filled solution-polymerized styrene-butadiene rubber (SSBR) compounds were investigated and application of the time-concentration superposition (TCS) principle to this system was verified. Master curves were obtained by shifting the frequency sweep rheological data of the filled compounds with respect to the unfilled SSBR. The master curves disclosed the existence of modulus plateaus in the low frequency region while the complex viscosity exhibited marked shear-thinning. The master tan  $\delta$  curves displayed maximum at a characteristic frequency that decreased with increasing filler volume fraction  $\varphi$ . The modulus and the frequency shift factors,  $A_G$  and  $A_{\omega}$ , were introduced into the TCS principle on the basis of strain amplification effect due to the presence of rigid undeformable SiO<sub>2</sub> particles as well as the constrained molecular motion of SSBR among the particles. Scaling relations were revealed to  $A_G$  and  $A_{\omega}$  as a function of  $\varphi$ . However, the  $A_G \sim \varphi$  relation did not follow the cluster-cluster aggregation (CCA) model that was usually suggested for particle suspensions or particle filled polymers. Influence of 3-octanoylthio-1-propyltriethoxysilane (NXT) as coupling agent to the dynamic rheological behaviors was also discussed. NXT did not influence the modulus plateaus and the shear-thinning index whereas it caused a reduction in characteristic relaxation time and marked increments in consistency and  $A_G$  in comparison with the NXT-free compounds.

**Keywords** Solution-polymerized styrene butadiene rubber (SSBR), Silica, Dynamic viscoelastic behavior, Time-concentration superposition (TCS) principle, Strain amplification factor

## 粘塑性金属材料高温蠕变实验及流变模型研究\*

罗迎社<sup>1</sup>,杨柳<sup>2</sup>,余敏<sup>1</sup>

(1 中南林业科技大学流变力学与材料工程研究所,湖南长沙410004;2 浙江林学院 园林学院,浙江临安311300)

**摘要:** 对三种不同的固体金属材料 Lc4 铝合金、TC11 钛合金及优质碳素结构钢(20#、35#)在高温下 进行了多组蠕变实验,根据实验曲线,采用修正的 Burgers 流变模型来描述这三种材料的高温蠕变行为, 建立了积分型蠕变本构方程和微分型应力应变本构关系,确定了蠕变积分核函数,并对由蠕变方程推 导的理论结果和实验结果进行了比较,理论值与实验值吻合较好。同时,利用蠕变实验数据,求出了 粘塑性材料本构方程中表征粘性性质的材料常数  $\gamma \langle \phi(F) \rangle$ ,并对这三种材料的粘性系数进行了比较分 析。

关键词:粘塑性材料;高温蠕变;金属;流变模型;粘性系数

中图分类号: 文献标识码: A

#### 1 引言

随着汽车、核电、航空等工业的迅速发展,对承受高温和复杂载荷的构件的可靠性要 求越来越高。对大多数金属而言,蠕变变形在室温环境下通常很小,可以忽略不计。但在高 温下,构件由于疲劳和损伤交互作用而发生随时间而变化的蠕变变形则必须考虑。蠕变通常 是指物体在恒定应力的作用下,应变随着时间的增长而增长的流变现象。一些重要的内外因 素,比如温度、时间、应力和组织结构等对金属的蠕变性能都有影响<sup>[1]</sup>。Brown 大学工程学 院Clifton R J.于 1985年在金属的塑性一文中把蠕变列为需要开展研究项目一览表的第一项, 并提议寻求蠕变的统一处理方法,通过微观与模拟相结合,将蠕变应力与基本机理研究结合 起来<sup>[2-3]</sup>。现代工业的发展和高温设备的广泛使用,赋予了金属蠕变问题研究更大的意义。 本文对三种不同的固体金属材料 Lc4 铝合金、TC11 钛合金及优质碳素结构钢在高温下进行 了多组蠕变实验,根据实验曲线,采用修正的 Burgers 流变模型来描述这三种材料的高温蠕 变行为,建立了积分型蠕变本构方程和微分型应力-应变本构关系,确定了蠕变积分核函数。 同时,利用蠕变实验数据,求出了粘塑性材料本构方程中表征粘性性质的材料常数,并对这 三种材料的粘性系数进行了比较分析。

2 实验方法

基金项目: 国家教育部科技重点项目(02103),湖南省教育厅科技重点项目(02A008),湖南省自科基金项目(03JJY3007)和湖南省优秀博士学位论文专项奖励项目(湘财教指[2003]48号)资助。

**作者简介:** 罗迎社(1954-),男,教授,博导,主要研究方向:固体流变学及其本构理论, E-mail:lys0258@sina.com

试验所用设备分别为仿英 T-48 型的国产 RD2-3 型和 RC-1230 型高温蠕变及持久强度试验机。试验材料为 Lc4 铝合金、TC11 钛合金及 20 号和 35 号优质碳素结构钢,统一加工成 Φ10\*100 试件,符合国标 GB/T2039-1997。然后将试件在不同温度不同应力水平下,进行多 组高温蠕变试验,实验曲线如图 1-4 所示。图 1 (a)为 Lc4 铝合金在同一温度水平(150℃)及不同应力水平(分别为 220MPa、230MPa、240MPa)的蠕变实验曲线,图 1 (b)为 Lc4 铝合金在同一应力水平(分别为 220MPa、230MPa、240MPa)的蠕变实验曲线,图 1 (b)为 Lc4 铝合金在同一应力水平(220MPa)及不同温度水平(分别为 145℃、150℃、155℃)下的蠕变实验曲线,图 2为 TC11在同一温度水平(550℃)及不同应力水平(分别为 343MPa、353MPa、363MPa)的蠕变实验曲线,图 3为 20 号钢在同一温度水平(500℃)及不同应力水平(分别为 130MPa、135MPa、140MPa)的蠕变实验曲线,图 4为 35 号钢在同一温度水平(500℃)及不同应力水平(分别为 140MPa、150MPa、160MPa)的蠕变实验曲线。











图 3 20 号钢的蠕变曲线(500℃),

#### 图 4 35 号钢的蠕变曲线 (500℃),

#### 3 实验结果分析

#### 3.1 蠕变本构方程的确定

蠕变曲线一般可以分作三个阶段,即过渡蠕变阶段、稳态蠕变阶段、加速蠕变阶段。当蠕变 进入加速阶段时,蠕变速率迅速上升,蠕变变形迅速发展,材料的内部组织可能发生突发性 破坏,即蠕变断裂。对于金属流变成形来说,断裂即意味着成形的失败,因此主要考虑前两 个阶段的变形。由上述三种材料的蠕变实验曲线可以看出,它们呈现一些共同的特点,其一, 在一定的温度下施加小的负载时,或者负载一定而温度较低时,由实验获得的曲线的特点表 现为具有恒定蠕变速度的第二蠕变阶段很长。这就为人们提供一种避免具有加速蠕变特性的 第三蠕变阶段直至断裂在全部实验期间可能根本不出现的蠕变极限应力和蠕变极限温度的 实验途径。此结论与 Griffiths W T.对于耐热镍铬合金所做的实验结果是相吻合的<sup>[4]</sup>。其二, 它们的第一阶段很短,第二阶段与 Burgers 模型蠕变曲线很相似,因此考虑采用修正的 Burgers 流变模型来描述它的蠕变行为。

图 5 为 Burgers 模型,该模型中没有塑性元件,因此,尽管该模型的蠕变曲线的走向 与材料的实验蠕变曲线的走向一致,但是对粘塑性金属材料来说它还不是最理想的模型。图 6 所示为修正的 Burgers 模型<sup>[3, 5-7]</sup>,其蠕变曲线的走向与 Burgers 模型一样,但它还包含了 一个塑性元件,体现了材料的粘塑性特征,所以选择用此模型。



对于修正的 Burgers 模型,其本构方程表达式如下<sup>[3]</sup>:

$$\varepsilon(t) = \frac{\sigma_0}{E_1} + \frac{\sigma_0}{E_2} \left[ 1 - \exp\left(-\frac{E_2}{K_2}t\right) \right] + \frac{(\sigma_0 - \sigma_s)}{K_3}t, \qquad \sigma_0 \ge \sigma_s$$

(1)

现以 TC11 材料为例,推导其蠕变本构方程表达式。 当应力水平  $\sigma_0$  为 343MPa 时,令t = 0,即有

$$\varepsilon_{0} = \frac{\sigma_{0}}{E_{1}}, \quad \varepsilon^{*}(t) = \frac{\sigma_{0}}{E_{1}} + \frac{\sigma_{0}}{E_{2}} + \frac{(\sigma_{0} - \sigma_{s})}{K_{3}}t$$
(2)

令 
$$\frac{\sigma_0 - \sigma_s}{K_3} = \eta$$
 其中 $\eta$ 为渐近线的斜率。根据实验数据可以确定该渐近线,因而

其斜率得以确定,当应力水平分别为 343MPa、353MPa 时所得到的蠕变曲线的渐近线的斜率分别为  $\eta_1 = 0.1928 \times 10^{-3} / \text{hr}$ 、  $\eta_2 = 0.2153 \times 10^{-3} / \text{hr}$ ,则有:

$$\begin{split} K_{3} &= \frac{\sigma_{0}^{1} - \sigma_{0}^{2}}{\eta_{1} - \eta_{2}} = \frac{10 \times 10^{6} \,\mathrm{Pa}}{0.0226 \times 10^{-3} \,/\,\mathrm{hr}} = 444.44 \,\mathrm{GPa} \cdot \mathrm{hr} \\ ( 3 ) \\ \sigma_{s} &= \sigma_{0}^{1} - K_{3} \eta_{1} = 343 - 444.44 \times 10^{3} \times 0.1928 \times 10^{-3} = 257.31 \,\mathrm{MPa} \\ ( 4 ) \\ &\Leftrightarrow t = 0 , \quad 则 \, \varepsilon_{0}^{*} = \frac{\sigma_{0}}{E_{1}} + \frac{\sigma_{0}}{E_{2}}, \quad 将式 \, E_{1} = \frac{\sigma_{0}}{\varepsilon_{0}} \, 代入 \, \exists : \end{split}$$

$$E_2 = \frac{\sigma_0}{\varepsilon_0^* - \varepsilon_0} = \frac{343 \times 10^6}{(3.8 - 3.52) \times 10^{-3}} = 1225 \text{GPa}$$
(5)

其中 $\varepsilon_0^*$ 为渐近线在 y 轴上的截距。求出 $E_1$ 、 $E_2$ 、 $K_3$ 、 $\sigma_s$ 后,现在只要再求出参数 $K_2$ , 再任取一组实验数据 $\varepsilon$ 、t代入式(1),便可以求出 $K_2 = 42654.895$ GPa·hr。 这样便可以确定应力水平为 343MPa 时的蠕变方程为:

$$\varepsilon(t) = 3.52 \times 10^{-3} + 0.28 \times 10^{-3} [1 - \exp(-0.0287t)] + 1.928 \times 10^{-4} t$$
(6)

采用同样的方法,Lc4 铝合金在应力水平为 220MPa 下的蠕变方程为  $\varepsilon(t) = 3.055 \times 10^{-3} + 0.223 \times 10^{-3} [1 - \exp(-0.90568 t)] + 1.288 \times 10^{-5} t$  (7)

表 1 为 TC11 钛合金蠕变方程推导的理论结果与实验结果的误差比较。在稳态蠕变阶段,两者的误差在 5% 以内,说明理论值与实验数据吻合的较好。

根据流变力学中的模型理论,我们可以求出推广的 Burgers 模型的微分型应力应变本 构关系为:

$$\sigma - \sigma_s + \frac{E_1(K_2 + K_3) + E_2 K_3}{E_1 E_2} \dot{\sigma} + \frac{K_2 K_3}{E_1 E_2} \ddot{\sigma} = K_3 \dot{\varepsilon} + \frac{K_2 K_3}{E_2} \ddot{\varepsilon}$$
(8)

将实验数据所求的各模型参数值代入式(8),便可以确定 TC11 钛合金在温度为 550℃, 应力水平为 343MPa 时的微分型应力应变本构关系。

$$\sigma - 2.57 \times 10^8 + 3.59 \times 10^3 \dot{\sigma} + 159 \ddot{\sigma} = 4.44 \times 10^{11} \dot{\varepsilon} + 1.55 \times 10^{13} \ddot{\varepsilon}$$
(9)

	过渡蠕变阶段			稳态蠕变阶段				
t 小时	0	2.5	4	15	26.5	30	48	62
蠕变实验值 ε(×10 <sup>−3</sup> )	3.52	4.43	4.7	6.51	8.5	9.1	12.67	15.88
模型理论值 $\varepsilon(\times 10^{-3})$	3.52	4.0214	4.322	6.51	8.778	9.465	12.98	15.48
误差值	0%	9.22%	8.04%	0%	3.27%	4.01%	2.45%	2.51%

#### 表1 实验值与理论值的误差比较

#### 3.2 蠕变积分核函数的确定

考虑某一物理体系或者力学体系,在不同时间  $\tau$  所受到的外界作用的影响延续到往后 某一确定时刻 t 的总效果。若这种影响不是相互耦合而是线性的,便可以用 Boltzmann 叠加 原理进行数学处理<sup>[7]</sup>。根据这一原理,若有某一应力  $\sigma = \sigma(t)$  作用于物体,我们可以将应力  $\sigma = \sigma(t)$  离散为一系列单个脉冲应力作用于物体,物体的变形即为这些脉冲应力作用的综 合效果。

$$\begin{cases} \sigma_1(t) = 0, \stackrel{\text{\tiny def}}{=} t < \tau \\ \sigma_1(t) = \sigma(\tau), \stackrel{\text{\tiny def}}{=} t \ge \tau \end{cases}$$

(10)

按 Boltzmann 叠加原理,此脉冲应力作(10)式的等价处理后所导致的应变为

$$\Delta \varepsilon(\tau) = \sigma(\tau) J(t-\tau) - \sigma(\tau) J(t-\tau - \Delta \tau) = \sigma(\tau) \Delta J(t-\tau)$$
(11)

其中, J(t)为蠕变柔量。当 $\Delta \tau \rightarrow 0$ 时有

$$d\varepsilon(\tau) = \sigma(\tau) \frac{\partial J(t-\tau)}{\partial \tau} d\tau$$
<sup>(12)</sup>

假定应力 $\sigma(t)$ 的作用时间是从 $-\infty$ 到t,并考虑到在t瞬时, $\sigma(t)$ 会产生瞬时应变

$$\begin{split} J_0\sigma(t) , J_0 \end{pmatrix} * 普 弹 柔 量 , 则 总 应 变 为 \varepsilon(t) = J_0\sigma(t) + \int_{-\infty}^t \sigma(\tau) \frac{\partial J(t-\tau)}{\partial \tau} d\tau \end{split} \end{split}$$
(13)  

$$\vdots K(t-\tau) = \frac{\partial J(t-\tau)}{\partial \tau} , \\ \eta \eta \delta \\ \varepsilon(t) = \frac{\sigma(t)}{E_0} + \int_{-\infty}^t \sigma(\tau) K(t-\tau) d\tau \qquad (14)$$

$$L 式 即 为 积 分型 的 - 般 蠕 变 本 构 方程 。 同理, 可以导出积 分型松弛 本 构 方程 \end{split}$$

$$\sigma(t) = E_0 \varepsilon(t) - \int_{-\infty}^t \varepsilon(\tau) R(t-\tau) d\tau$$
(15)

其中 $K(t,\tau)$ 、 $R(t,\tau)$ 分别为方程式(14)、(15)的核函数,简称积分核,它们是反映流变材料的流变特性的特征函数。我们对材料进行蠕变实验时,应力为某一恒定的应力 $\sigma_0$ ,作用的初始时间为 $t_0 = 0$ ,所以其蠕变型的流变积分方程为

$$\varepsilon(t) = J_0 \sigma_0 + \sigma_0 \int_0^t K(t-\tau) d\tau$$

(16)

令
$$t - \tau = x$$
,则 $\tau = 0$ 时, $x = t$ ;  $\tau = t$ 时, $x = 0$ ;  $d\tau = -dx$ 。上式可以变为  
 $\varepsilon(t) = J_0\sigma_0 - \sigma_0\int_t^0 K(x)dx = J_0\sigma_0 + \sigma_0\int_0^t K(x)dx = J_0\sigma_0 + \sigma_0\int_0^t K(t)dt$  (17)

令x = t, 上式两边对时间t求导数有 $\varepsilon(t) = \sigma_0 K(t)$  所以

$$K(t-\tau) = \frac{\varepsilon(t-\tau)}{\sigma_0}$$
(18)

将材料 Lc4 铝合金在应力水平为 220MPa 下的蠕变方程式(7)代入上式,则其蠕变积分核 函数为:

$$K(t-\tau) = 5.855 \times 10^{-14} + 9.180 \times 10^{-13} \exp[-0.90568(t-\tau)]$$
(19)

### 3.3 粘塑性材料本构方程材料参数<sup>7</sup>的确定

利用塑性势理论,将粘塑性应变率 $\dot{arepsilon}_{ij}^{vp}$ 与粘塑性势Q的关系表示为<sup>[3,8,9]</sup>:

$$\dot{\varepsilon}_{ij}^{vp} = \gamma \langle \phi(F) \rangle \frac{\partial Q}{\partial \sigma_{ij}} \tag{20}$$

其中, $\gamma\langle \phi(F) \rangle$ 为材料常数,尖括号 $\langle \phi(F) \rangle$ 的意义是

 $\langle \phi(F) \rangle = \phi(F)$  (当 F > 0 时)有粘塑性流动

99

$$\langle \phi(F) \rangle = 0$$
 (当 $F \le 0$ 时)无粘塑性流动

函数  $\phi(F)$  根据材料特性试验确定。采用关联流动法则,取Q = F,则式(20)成为

$$\dot{\varepsilon}_{ij}^{\nu p} = \gamma \langle \phi(F) \rangle \frac{\partial F}{\partial \sigma_{ij}}$$
<sup>(21)</sup>

由于

$$\frac{\partial F}{\partial \sigma_{ij}} = \frac{\partial \sqrt{J_2'}}{\partial \sigma_{ij}} = \frac{\sigma_{ij}'}{2\sqrt{J_2'}}$$
(22)

代入到(22)式,得

$$\dot{\varepsilon}_{ij}^{vp} = \gamma \langle \phi(F) \rangle \frac{\sigma'_{ij}}{2\sqrt{J'_2}}$$
<sup>(23)</sup>

将上式两端平方,则有

$$\dot{\varepsilon}_{ij}^{\nu p} \dot{\varepsilon}_{ij}^{\nu p} = \gamma^2 \left\langle \phi(F) \right\rangle \frac{\sigma_{ij}' \sigma_{ij}'}{4J_2'} \tag{24}$$

式中 $\sigma_{ij}$ 、 $\sigma'_{ij}$ 分别为应力张量分量和偏应力张量分量。注意到 Mises 材料的等效应力和等效 应变率分别为

$$\overline{\sigma} = \sqrt{3J_2'} = \sqrt{\frac{3}{2}\sigma_{ij}'\sigma_{ij}'}$$
(25)

$$\dot{\bar{\varepsilon}}^{\nu p} = \sqrt{\frac{2}{3}\dot{\varepsilon}^{\nu p}_{ij}\dot{\varepsilon}^{\nu p}_{ij}} \tag{26}$$

因此,式(24)可改写为

$$\frac{3}{2} \left( \dot{\overline{\varepsilon}}^{\nu p} \right)^2 = \gamma^2 \left\langle \phi(F) \right\rangle^2 \frac{\frac{2}{3} \cdot \overline{\sigma}^2}{4 \cdot \overline{\sigma}^2/3}$$
(27)

由此得

$$\gamma \langle \phi(F) \rangle = \sqrt{3} \bar{\varepsilon}^{vp} \tag{28}$$

#### 3.4 三种不同材料粘性系数的比较与分析

图 7 为 TC11 钛合金在温度为 550℃,应力分别为 343MPa、353MPa、363MPa 时的 $\sigma - \gamma$ 关系图,图 8 为 Lc4 铝合金在温度为 150℃,应力分别为 220MPa、230MPa、240MPa 时的 的 $\sigma - \gamma$ 关系图,图 9 为 20 号钢在温度为 500℃,应力分别为 130MPa、135MPa、140MPa 时的的 $\sigma - \gamma$ 关系图,图 10 为 35 号钢在温度为 500℃,应力分别为 140MPa、150MPa、160MPa 时的的 $\sigma - \gamma$ 关系图。将这三种固体材料的粘性系数曲线进行比较,可以发现它们有一个共 同的特点,即当温度不变,表征材料粘性性质的 $\gamma\langle \phi(F) \rangle$ 随着应力的增加而增大。当应力增大时,蠕变曲线变得越来越陡,从而导致等效应变率 $\dot{\varepsilon}$ 增大,因此 $\gamma$ 值也增大。



应力与表征材料粘性性质的系数 γ 成线性关系,这是因为忽略了 ё 项,以及实验应力 差较小的原因。它们的最大差异在于,由于三种材料的材质不同,即材料成分不同,在相变 温度内,γ值分别相差一个数量级,碳素钢的粘性最大,钛合金次之,铝合金的粘性最小。 可见,在进行材料的流变加工时,应该根据不同的材料选用不同的润滑剂。上述研究结果对 新型润滑剂的研发也有一定的指导意义或参考价值。

#### 4 结论

(1). 对三种不同的固体金属材料 TC11 钛合金、Lc4 铝合金及优质碳素结构钢(20#、35#) 在高温

101

下进行了多组蠕变实验,根据实验曲线,采用修正的 Burgers 流变模型来描述这三种材料的高温蠕变行为,建立了积分型蠕变本构方程和微分型应力应变本构关系。确定了蠕变积分核函数,并对由蠕变方程推导的理论结果和实验结果进行了误差分析。

- (2).利用蠕变实验数据,确定了粘塑性材料本构方程中表征粘性性质的材料常数γ⟨φ(F)⟩, 并对这三种材料的粘性系数进行了比较分析,结果表明:它们有一个共同的特点,即当 温度不变,γ⟨φ(F)⟩随着应力的增加而增大;它们的不同点在于,在相变温度内,γ值 分别相差一个数量级,碳素钢的粘性最大,钛合金次之,铝合金的粘性最小。
- (3). 材料的粘性与材质类别、应力水平、变形速率和温度等诸多因素相关,并非一成不变的 常数。这对于在材料加工领域研究粘性、摩擦和润滑之间的相互关系、对于新型材料 设计、表面改性、新型润滑剂开发有一定的参考价值和指导意义。

#### 参考文献:

- [1] 穆霞英, 蠕变力学[M], 西安: 西安交通大学出版社, 1990, 1~5。
- [2] Clifton R. J. Plasticity of metal[J], Appl. Mech. Rev., 1985, 38(10):1261-1263.
- [3] 罗迎社,金属流变成形的理论、实验与应用研究[D],长沙:国防科学技术大学研究生院,2000.
- [4] A.撒利著,李文澜,王鸿渐等译,金属蠕变与耐热合金,北京:国防工业出版社,1965.
- [5] Luo Yingshe, Hu Yungui, Zhou Jianping, Li Suyang, Creep experimental research on aluminum alloy Lc4[C], XIIIth International Congress on rheology, edited by D M Bingding, N E Hudson, etc., Universities Design & Print Unit, Glasgow, UK, 2000, Vol.4, 368~370.
- [6] Yang Liu, Luo Yingshe, Tang xiaodi, Rheological properties of carbon constructional quality steels[J], Journal of Central South University of Technology, 2007, Vol.14, 285~288.
- [7] 刘雄,岩石流变学概论[M],北京:地质出版社,1994,121~125。
- [8] 杨绪灿,杨桂通,徐秉业编著,粘塑性力学概论[M],北京:中国铁道出版社,1985
- Y.S. Luo, K. Donda and Z. Wang, Experimental solution for viscocity coefficient of solid alloy material[J], Int. J. of Applied Mechanics and Engineering, 2003, Vol.8, 271~276.

## Research on creep experiments under high temperature and rheological model of visco-plastic metal materials

Luo Yingshe<sup>1</sup>, Yang Liu<sup>2</sup>, Yu Ming<sup>1</sup>

(1. Institute of Rheological Mechanics and Material Engineering, Central South University of Forestry and Technology, Hunan Changsha 410004, China;

2. School of Landscape Architecture, Zhejiang Forestry University, Zhejiang, Lin-an 311300,

China)

**Abstract:** The creep experiments under high temperature have been done on Lc4 aluminum alloy, TC11 titanium alloy and the carbon constructional quality steels (20 steel, 35 steel). The integral creep constitutive equation and differential stress-strain constitutive relationship can be established according to relevant rheological model named revised Burgers and the integral core of the creep has been achieved through the experiments. Comparing the calculation results conducted from the model with the experiment results, they were in good agreement. Moreover, the coefficient  $\gamma \langle \phi(F) \rangle$  related with viscosity of visco-plastic materials were obtained through creep experiments' datum. The viscosity coefficients of the three kinds of materials were also compared and analyzed. **Keywords:** visco-plastic material; high temperature creep; metal; rheological model; viscosity

coefficient

## Dynamic Rheological Behavior and Morphology Near Phase-Separated Region for A LCST-type of Binary Polymer Blends

DU Miao GONG Jianhua ZHENG Qiang\*

(Department of Polymer Science and Engineering,

Zhejiang University, Hangzhou, China, 310027)

Abstract: The dynamic rheological properties and morphology in the vicinity of phase-separated region for poly (methyl methacrylate) (PMMA) /poly (styrene-co-acrylonitrile) (SAN) blends with lower critical solution temperature (LCST) behavior were investigated. When temperature was above the phase separation temperature, i.e. cloud point  $(T_c)$  for some PMMA/SAN blends, the slope of plotting  $\log G'$  versus  $\log \omega$  decreased at low frequencies (terminal region), indicating the appearance of phase-separation and existence of heterogeneous structure. We employed a model dealing with complex modulus of the two phases mixture proposed by Kopnistos et. al for describing the dynamic rheological behaviors of PMMA/SAN blends, according to the assumption that the interfacial tension between the matrix and the dispersed phase was independent of local shear and variation of interfacial area, and that the dispersed spherical droplets were nearly monodispersed. It is found that the predicted results were in qualitative agreement with the experimental data of this study. The ratio of interfacial tension  $\alpha$  to the size of dispersed phase R,  $\alpha/R$ , was obtained for 80/20 and 60/40 PMMA/SAN blends, and the two different morphology were also observed. It is believed that the decrease of loss tangent (  $tan\delta$  ) was resulted from the formation of domains rich in PMMA or SAN component of the blends because of decreasing the friction force between the two domains in the molten state. This behavior was attributed to be the structure change from homogeneous to heterogeneous.

Keywords: PMMA/SAN blend; Phase-separation; Dynamic rheological behavior; Morphology

#### 1. Introduction

The rheology of multi-component polymer systems, such as polymer blends and block copolymers, has become the attractive interest because of the challenging physical problems and the increasing technological applications behind. To date, most of the work addressed the rheological behavior to immiscible polymer blends, which typically exhibited characteristics concerning processing. However, a few attentions has been paid to the rheological properties of homogeneous systems, especially for the lower critical solution temperature (LCST)-type polymer blends<sup>[1,2]</sup>.

<sup>\*</sup> To whom correspondence should be addressed Tel.: +86-571-87952522; Fax: +86-571-87952522

E-mail: zhengqiang@zju.edu.cn

It is well-accepted that some specific intermolecular interaction including hydrogen bond,  $n-\pi$  complex and Lewis acid-base interactions are sufficient to promote the formation of single-phase polymer blends. However, the occurrence of a stable single-phase polymer blend is not restricted to the systems above. There exist miscible polymer blends in which the miscibility derives from the so-called *"repulsion effect"*. In these blends at least one component is a random copolymer with miscibility over a range of copolymer compositions even though combination of the corresponding homopolymers are immiscible<sup>[3]</sup>. A blend composed of a homogeneous polymer, poly (methyl methacrylate ) ( PMMA ), and a random copolymer, poly ( styrene-co-acrylonitrile ) ( SAN ) can be taken as an example since it exhibits LCST phase-separation upon heat-treatments. When temperature changes, it is possible to obtain blends with various phase morphology (single or separated) and different viscoelastic properties<sup>[4]</sup>.

Rheological measurements, especially dynamic testing, have been the primary characterization method for polymer blends<sup>[5, 6]</sup>. Based on the rheological measurements, many fingerprints can be found out to infer qualitatively or quantitatively the critical point of phase-transition in polymers. Especially, the second plateau on the curves for rheological functions of frequency ( $\omega$ ) at low  $\omega$ range (terminal range) is thought to be a sign for the deviation level of viscoelastic behavior from the linear theory. The above phenomena have been responsible for the rheological properties of the phase-separation for polymer blends <sup>[7, 8]</sup>. In our previous work <sup>[9]</sup>, we have reported that the change of dynamic storage modulus (G') against  $\omega$  could be used to judge whether the phase separation takes place in PMMA/SAN blend system or not, on the basise of whether the relationship between G' or dynamic loss modulus (G'') and  $\omega$  follows  $G' \propto \omega^2$  and  $G'' \propto \omega$  or not. However, this method sometimes was not so effective when the "second plateau" was not obvious. The change of dynamic modulus with  $\omega$  for a blend system could be also estimated through a model function <sup>[10]</sup>, but up to now there has been few literatures concerning the dynamic viscoelasticity behavior for PMMA/SAN blends system near phase separation. In addition, even the loss tangent (tan $\delta$ ) is understood to be strongly affected by the degree of phase homogeneity, the change of tan $\delta$  caused by phase-separation in PMMA/SAN has not been reported hitherto.

In this paper, we try to estimate quantitatively the dynamic viscoelasticity and morphology evolution in the vicinity of phase-separation region for PMMA/SAN blends by investigating the dynamic rheological behavior.

#### 2. Experimental

The materials used in this study were polymethyl methacrylate(PMMA) (LG chemical Ltd. Korea with  $\overline{M}_n = 3.8 \times 10^4$ ,  $\overline{M}_w / \overline{M}_n = 2.1$ ) and poly(styrene-co-acrylonitrile) (SAN)
(Chimei Corporation (Taiwan), AN = 28 wt%,  $\overline{M}_n = 6.4 \times 10^4$ ,  $M_w/M_n = 1.9$ ).

PMMA/SAN films for small angle laser light scattering (SALLS) observation were prepared by dissolving the two component polymers in dichloroethane (CH<sub>2</sub>ClCH<sub>2</sub>Cl) at a weight fraction of 5%, and then the solution was cast on the surface of a microscope slide preheated to 30 °C. After the solvent evaporated at the ambient environment, the samples were further dried in a vacuum oven at 100 °C for at least 24 h to ensure no residual solvent.

The PMMA/SAN blends for rheological measurements were obtained by dissolving the blends in methyl ethyl ketone (CH<sub>3</sub>COCH<sub>2</sub>CH<sub>3</sub>) at a weight fraction of 15 %. After the solvent evaporated at ambient environment over a night, the films were heated for 24 h at 60 °C, 80 °C, 100 °C and 120 °C, respectively. For ensuring complete removal of solvents, the films were then dried in a vacuum oven at 140 °C for 48 h. Weight loss of the samples was monitored until they reached a constant weight. The films with thickness of 80 ~100  $\mu$ m were stacked up and compression-moulded into specimen disc with a diameter of 25 mm and a thickness of 1.5 mm at 10 MPa and below 150°C for rheological tests.

The cloud point ( $T_c$ ) of each sample was detected by SALLS. A piece of the blend film was inserted into a hot chamber which was kept at a constant temperature and lived there 12 h for annealing. When the scattering ring was observed on the screen, we ascertained that the blend was located in the immiscible region in the  $T_c$ 's curve. When no discernible change with the annealing under above conditions was detected, the film was further annealed at the same temperature for 36 h. In case the film was still clear and no phase-separation was confirmed on the screen after samples were exposed to annealing for a long time, we ascertained that the blend was in the miscible region.

The rheological tests were conducted on an Advance Rheometric Expansion System (2ARES-9A) with parallel plate geometry of 25 mm in diameter. The frequencies were from  $10^{-2}$  to  $10^2$  rad·s<sup>-1</sup>. Depending on the given temperature from 150 °C to 190 °C, the strain amplitude was taken between 3.0 % and 20 % to obtain a high torque. All applied strain were in the linear viscoelastic range.

A transmission electron microscopy (TEM) was used to observe the morphology of the blends. The samples were stained using osmium tetroxide for 24 h. TEM micrographs of sections with thickness of 200 nm were taken with a JEM-1200EX TEM.

#### 3. Results and discussion

3.1. Effect of phase-separation on dynamic viscoelastic response

It is well-known that the measuring dynamic mechanical properties under long time relaxation

is an appropriate method to obtain information on miscibility or immiscibility of polymer systems, because the dynamic viscoelastic responses, under this condition, are sensitive to the changes of structure and morphology for polymers <sup>[11]</sup>. Actually, it is impossible to approach a infinite relaxation time (or infinitesimal frequency) condition. Hence, many researchers characterized the miscibility or phase-separation of multi-component and/or multi-phase polymer systems according to the change of the intrinsic properties in relatively low  $\omega$  region <sup>[12]</sup>.

**Table 1** The determined rheological demixing temperature  $(T_b)$ and cloud point ( $T_c$ , SALLS) of PMMA/SAN blends

PMMA/SAN	$T_b/ {}^oC$	T <sub>c</sub> / <sup>o</sup> C
20/80	>200	>200
40/60	185	190
60/40	165	173
80/20	165	163

The G' and G'' for the component polymer and for the 20/80, 40/60, 60/40 and 80/20PMMA/SAN blends were measured as a function of  $\omega$  at different temperatures from 150 to 190 °C by a step of 10 °C. For clarity, the discussion in the present paper was mainly focused on the blends with compositions 60/40 and 80/20. Fig. 1 (a), (b) and (c) present the typical isotherms of G' for PMMA, 60/40 and 80/20 PMMA/SAN blends. It can be seen that at low temperatures, the blends (b and c) behave similarly to a homogenous polymer PMMA (a) with a rubbery plateau followed by a continuous decrease of G' as a function of  $\omega$ . Such a decrease corresponds to the beginning of the terminal region. But it is impossible to reach this terminal region at low temperatures due to the limitation of the instrument exposed to a very low  $\omega$ . In contrast, at high temperatures, G' exhibits a shoulder, namely "second plateau", together with an increasing width with the increase of temperature in the low  $\omega$  region. These phenomena were reported for polystyrene/polyvinyl methyl ether (PS/PVME) blend, and the presence of the "second plateau" in G' was assigned to phase-separated domains of PS and PVME<sup>[13, 14]</sup>. On the other hand, this behavior has been believed to be the result of change from homogeneous to heterogeneous structure<sup>[15]</sup> and was designated the fingerprint for the presence of phase-segregated domains<sup>[16]</sup>. The thermorheological complexity of polymer blends near phase boundaries is due to the large concentration fluctuation in the homogeneous region in the vicinity of phase-separation and in the various morphologies in the phase separated region. Similar observations hold for the behavior of G'' as well, but much reduced sensitivity appears (a', b' and c' of Fig. 1). We have reported that the

change of G' against  $\omega$  could be used to judge whether the blend system appear phase separation or not <sup>[9]</sup>. The determined rheological demixing temperatures( $T_b$ ) were in satisfactory agreement with those obtained from turbidity,  $T_c$ , as given in Fig. 2 and Table 1. Because it was very difficult to obtain the accurate of 90/10 or 10/90 PMMA/SAN blends by means of SALLS, Fig. 2 only gave the  $T_c$  of 40/60, 60/40 and 80/20 PMMA/SAN blends.



Fig. 1 Dynamic storage modulus (G') and loss modulus(G") as a function of frequency (ω) for (a, a') PMMA,
(b, b') 60/40 PMMA/SAN and (c, c') 80/20 PMMA/SAN blends at different temperatures.



**Fig. 2** The cloud points  $(T_c)$  for PMMA/SAN blends.



**Fig. 3** The temperature dependence of terminal slopes for (1) PMMA, (2) 20/80PMMA/SAN, (3) 40/60PMMA/SAN, (4) 80/20PMMA/SAN and (5) 60/40 PMMA/SAN blends.

In order to characterize the phase-separation of PMMA/SAN blends more clearly, some mathematical treatments are made here. The terminal slope of plotting logG' versus log $\omega$  in the lower frequencies for PMMA and PMMA/SAN blends at different temperatures are shown in Fig. 3. It is very interesting that the terminal slope for PMMA increases with the increase of temperature. According to linear viscoelastic theory, i.e.  $\log G' \propto 2\log \omega$  at the terminal region for homogeneous polymer melts, it is clear that the terminal slopes of plotting  $\log G'$  versus  $\log \omega$  for PMMA at higher temperatures approach 2.0. But for PMMA/SAN blends, the relationship between the terminal slope of the plotting and temperature changes, which is relevant to the phase-separation of the blends. Similar to that of PMMA, the terminal slope of this increases with the increase of temperature for 20/80 PMMA/SAN blends, indicating the blend system is homogeneous under experimental conditions and the results obtained coincides with those observed by SALLS ( $T_c > 200$  °C).

For other PMMA/SAN blend, 40/60, 80/20 and 60/40 PMMA/SAN, as shown in Fig. 3, the terminal slope of plotting  $\log G'$  versus  $\log \omega$  first increase and then decrease with the increase of temperature. These phenomena are believed to be the results of phase-separation for polymer blends. According to Fig. 2,  $T_c$  of 80/20 PMMA/SAN blends is 163 °C. Furthermore, from Fig. 3, it can be seen that the terminal slope of plotting  $\log G'$  versus  $\log \omega$  decreases when temperature is above 160 °C, implying that the phase separation of the blend took place and became heterogeneous.



**Fig. 4** Evaluation of the rheological behavior of the phase-separated 80/20PMMA/SAN blends at 180 °C: experimental data (*open symbols*),  $G'(\Box)$  and  $G''(\circ)$ ; emulsion model predictions from Eq.(1) and Eq.(2) for  $\alpha/R = 1000$  Pa (*solid line*); model predictions for  $\alpha/R = 0$  (*dashed lines*).



**Fig. 5** Evaluation of the rheological behavior of the phase-separated 60/40PMMA/SAN blends at 180 °C: experimental data (*open symbols*),  $G'(\Box)$  and  $G''(\circ)$ ; emulsion model predictions from Eq. (1) and Eq. (2) for  $\alpha/R = 1000$  Pa (*solid lines*); model predictions for  $\alpha/R = 0$  (*dashed lines*).

#### 3.2. Quantifying the rheological characteristics of phase-separated PMMA/SAN blends

In phase-separated region, the time-temperature superposition (TTS) principle could no longer be applied in the terminal region, associating with the enhanced moduli, as reported in our previous work<sup>[17]</sup>. However, this complex viscoelastic behavior in the two-phase region could be quantitatively analyzed by utilizing a theoretical approach to the rheology of emulsions with incompressible viscoelasticity. Concerning description of the rheological behavior for incompatible polymer blends in the molten state<sup>[18]</sup>, in which a general phenomenon observed was the substantial increase of elasticity in the terminal region, it is recognized that this increase could be described by constitutive equations for emulsions of two Newtonian liquids<sup>[19]</sup> or emulsions of two viscoelastic fluids <sup>[20]</sup>; and furthermore the latter could be better for accounting for behavior at the higher  $\omega$  as well. Hence, it was used for the case of immisicible polymer blends. In this work we employ essentially this approach in order to quantify the rheological characteristics of phase-separated PMMA/SAN blends. These systems are considered as emulsions of viscoelastic incompressible materials, in which the "suspended" particles forming the dispersed phase are assumed to be nearly spherical and their deformation remained small, i.e. located in the limits of linear viscoelasticity. The pronounced elasticity at low  $\omega$  is actually attributed to the interfacial tension. Furthermore, according to assumption by Kopnistos *et.*  $al^{[10]}$  that the interfacial tension between the matrix and the dispersed phase is independent of local shear and variation of interfacial area and that the dispersed spherical droplets are nearly monodisperse, the complex modulus of the two phase emulsion,  $G^*(\omega)$ , could be expressed as <sup>[17]</sup>

$$G^*(\omega) = G^*_m(\omega) \frac{1 + 3\phi H(\omega)}{1 - 2\phi H(\omega)} \tag{1}$$

in which,  $H(\omega)$  is given as

$$H(\omega) = \frac{4\frac{\alpha}{R}(2G_{m}^{*}(\omega) + 5G_{i}^{*}(\omega)) + (G_{i}^{*}(\omega) - G_{m}^{*}(\omega))(16G_{m}^{*}(\omega) + 19G_{i}^{*}(\omega))}{40\frac{\alpha}{R}(G_{m}^{*}(\omega) + G_{i}^{*}(\omega)) + (2G_{i}^{*}(\omega) + 3G_{m}^{*}(\omega))(16G_{m}^{*}(\omega) + 19G_{i}^{*}(\omega))}$$
(2)

where the subscripts m and i refer to the matrix and dispersed phase (inclusion), respectively;  $\alpha, \phi$ and R are the interfacial tension, and the volume fraction and size of the dispersed phase, respectively. This model can be generalized to the case of polydispersed inclusions and also reduced to a number of useful simpler models [18]. However, we simply employed the general formula above for monodispersed inclusions. From Eq. (1) and Eq.(2) the modulus of the emulsion can be estimated only if the corresponding moduli of the two constituents are known. According to the phase diagram as shown in Fig. 2, the phase-separated blends in the temperature region measured will never actually consist of pure PMMA or pure SAN domains, but consist of PMMA-rich and SAN-rich domains with compositions determined by the tie lines of the phase diagram. Hence we interpret the inclusions and matrix of the emulsion as these domains, into which a phase-separated blend of a given concentration can be decomposed, on the basis of its phase diagram (Fig. 2). More specifically, we examined the 80/20 PMMA/SAN blends at 180 °C, which can be considered to consist of pure PMMA matrix and 60/40 PMMA/SAN inclusions. According to the above model with one adjustable parameter, i.e. the ratio  $\alpha/R$ , we can obtain the results as depicted in Fig. 4. The predictions are dependent on  $\alpha/R$  and are in qualitative agreement with the experimental data in the whole  $\omega$  region, especially with respect to change of the slopes observed at low  $\omega$ . Furthermore, for a value of  $(\alpha/R)=0$ , corresponding to a dispersion of incompressible Hookean inclusion in an incompressible Hookean matrix, the quantitative agreement is believed to be considerably reasonable. Indeed, the results from the model reveal higher sensitivity to the elastic modulus; but it is considered to be satisfactory even though it gives a rather rough assumption concerning the dispersed phase. The limitation involving in the assumption of spherical monodisperse droplets is dealt with the fact that the temperatures

investigated (referring to Fig. 2) were near the phase boundary.

The more interesting situation is the case of the 60/40 PMMA/SAN blends at 180 °C, which is thought as inclusions of PMMA-rich spherical domains of constant size with concentration 100% PMMA (pure PMMA) dispersed in a matrix of SAN-rich domains with concentration 60% SAN (40/60 PMMA/SAN) on the basis of phase diagram (Fig. 2). Fitting with Eq.(1) and Eq.(2) reveals satisfactory results. Although the case of  $(\alpha/R) = 0$  gives mathematically slightly better results, the value  $(\alpha/R) = 1000$  is considered to be the optimum fitting parameter. However, in this case, as depicted in Fig. 5, the model could not satisfactorily capture the region of enhanced moduli and the subsequent terminal flow in this experiment. It is evident that  $(\alpha/R)$  is a critical parameter, which depends strongly on the state of the phase-separated blends, including composition, temperature and time. It is noted that the dispersed phase could be either PMMA-rich or SAN-rich domains on the basis of the blend composition given in phase diagram. The general results reveal that the linear viscoelastic behavior of a phase-separated binary polymer blends correspond to that of an emulsion of two incompressible viscoelastic fluids, and thus it can be described by the relevantly simplified model. This suggests an analogy of viscoelastic properties between the time-dependent situation of a phase-separated blends and an emulsion of incompressible viscoelastic fluids.





Fig. 6 TEM photos of (a) 80/20 and (b) 60/40 PMMA/SAN blendsannealed at 180 °C for 30 min.

Fig. 6 demonstrates TEM photos of 80/20 and 60/40 PMMA/SAN blends annealed at 180 °C for 30 min. It should be noted that the annealing temperature 180 °C is above  $T_c$  of the two blends; in other word, phase-separation of the two blends had taken place at 180 °C. It is very interesting

that there is blurry interphase between the dispersed phase and matrix for 80/20 PMMA/SAN, but clear phase boundary for 60/40 PMMA/SAN. These phenomenon are in agreement with the  $\alpha/R$  value obtained from the above model. For 80/20 PMMA/SAN blends, the  $\alpha/R$  value is closed to zero, indicating that the two components after annealing are miscible to some extent and appear a blurry interphase. However, for 60/40 PMMA/SAN , the value of  $\alpha/R$  can be considered as 1000, indicating that the two components of the dual phases are immiscible and comparatively clear phase boundary.

#### 4. Concluding remarks

The thermorheological complexity of polymer blends near phase boundaries is resulted from large concentration fluctuations in the homogeneous region in the vicinity of phase separation and in the various morphologies in the phase separated region. The decreases in terminal slope of plotting  $\log G'$  versus  $\log \omega$  when temperature is above cloud point( $T_c$ ) for PMMA/SAN blends indicate occurrence of phase-separation of the blends. G' appears much more thermorheological complexity than that of G''. The viscoelastic properties for the phase-separated blends can be interpreted on the basis of a simplified Kopnistos's model for describing the rheology of phase-separated blends is rather complicated and strongly related to the temperature, time and composition. Further studies of morphology evolution near phase-separation region for PMMA/SAN blends with various compositions should be carried out in detail in our future work.

#### Acknowledgements

This work was supported by the National Natural Science Foundation of China (Grant 20304014), Special Funds for National Science Funds for Distinguished Young Scholars (Grants 50125312) and Special Founds for Major State Basic Research Projects, China (Grant No. G1999064800).

#### References

- [1] Volker E. Macromolecules 1995; 28:6219
- [2] Harold L S, Paul M, Shymon R. Macromolecules 1983; 16: 757
- [3] Kleintjens L A Integration of Funamental Polymer Science and Technology, London and New York: Elsevier Appl Sci Pub, 1985
- [4] Bousmina M, Lavoie A, Riedl B. Macromolecules 2002 ; 35: 6274
- [5] Onogi S, Masuda T, Kitagawa, K. Macromolecules 1970; 3(2): 109

- [6] Zheng Q, Zhao T J. Chinese J Mater Res 1998; 12(3): 225
- [7] Han C D. Multiphase Flow in Polymers Processing. New York: Academic Press, 1981.
- [8] Han J H, Feng C C, Li D J, Han C D. Polymer 1995; 36(12): 2451
- [9] Zheng Q, Du M, Yang BB, Wu G. Polymer 2001; 42: 5473
- [10] Kopnistos M, Vlassopoulas D, Anastasiadis S H, Stammer A. Euro Phys Lett 1996; 34: 513
- [11] Kopnistos M, Hinrichs A, Vlassopoulas D, Anastasiadis S H, Stammer A, Wolf B A. Macromolecules 1996; 29: 7155
- [12] Masuda T, Takahashi M. Kobunshi 1993; 42: 734

[13] Carreau P J, Bousmina M, Ajji A. Rheological Properties of Blends, Facts and Challenges, In Pacific Polymers. New York: Springer-Verlag, 1994

- [14] Kim J K, Son H W. Polymer 1999; 40: 6789
- [15] Onogi S, Matsumoto T. Polym Eng Rev 1981; (1): 45
- [16] Ajji A, Choplin L, Prud'Homme R E. J Polym Sci Part B: Polym Phys 1991; 29: 1573
- [17] Du M, Wang L Q, Yang B B, Song X B, Zheng Q. Chem J Chinese Univ 2002; 23(5): 961
- [18] Gracbling D, Muller R, Palierne J F. Macromolecules 1993; 26: 320
- [19] Schowalter W R, Chaffey C E, Brenner H. J Colloid Interface Sci 1968; 26: 152
- [20] Oldroyd J G. Proc. R. Sco. London 1953; A218: 122

# Mechanical and Electrical Properties of Hydrous Electrorheological Elastomers Based on Gelatin/ Glycerin/Water Hybrid

### Lingxiang Gao, Xiaopeng Zhao

Department of Applied Physics, Institute of Electrorheological Technology 141#, Northwestern Polytechnical University, Xi'an 710072, People's Republic of China

Received 27 June 2006; accepted 6 August 2006 DOI 10.1002/app.25818 Published online in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** Aimed at improving the stability of geometrical shape, mechanical performance, and particles dispersion of electrorheological (ER) hydrous elastomers, a new gelatin water-based elastic gels containing starch particles were prepared under an applied dc electric field, and their ER effects were described with the compression modulus and the electric resistivity. The result demonstrates that the mechanical and electrical properties of the ER elastomers are dominated by an externally applied electric field as well as the weight fraction of particles. On comparing with the same chemical composition, elastomers cured without a field and with barium titanate/gel-

atin water-based elastomer, some conclusions are suggested: the object elastomer has stronger responses to a field than the same chemical composition elastomer, especially with higher weight fractions of particles. The object elastomer has steady geometrical shape and mechanical performance because of the addition of glycerin into the matrix, and has a better dispersion of particles. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 1738–1743, 2007

**Key words:** electrorheological effect; water-based elastomer; compression modulus; electric resistivity

#### **INTRODUCTION**

Electrorheological (ER) materials possess electrically controllable properties in mechanics, electrics, and optics.<sup>1-4</sup> Owing to the fact that electric field can be obtained and controlled expediently, ER materials have many applications in actuators, dampers, clutches, high power vibrators, torque transducers, and artificial muscle.<sup>5–8</sup> ER elastomer is a composite elastic gel, which consists of polarizable particles dispersed in chemical crosslinked network of organic macromolecule.<sup>7–9</sup> In the network, as matrix's solid-like nature, particles are restricted and the congregation of particles are eliminated. Consequently, the instability of the ER effect, which is caused by the particles' congregation in ER fluid, is improved.<sup>10,11</sup> At the same time, the interaction among the polarized particles under the applied electric field induces the elasticity change of the composite elastic gel, and then the elasticity change induces a notable ER effect. In addition, the shape

and size of ER elastomer can be designed for the practical requirement. Now, the advantages of ER elastomers have attracted a lot of attention to use them to produce mechanical devices.

In previous reports, a series of anhydrous macromaterials such as polysilicanes have been used as elastomer matrices,<sup>12</sup> but they have drawbacks e.g., long synthesis time and high-cost. ER elastomers with hydrous matrices have rarely been noticed. In our previous studies, we synthesized barium titanate/gelatin hydrous ER elastomers with gelatin/ water hybrid as a matrix.<sup>13</sup> Compared to anhydrous elastomers, the ER elastomers have some advantages, for instance, they are simple and convenient to synthesize, they have marked ER effect, low-cost, and are friendly to environment. On the other hand, they have some shortages as well, such as the low stability of geometrical shape and mechanical performance because of the water in matrix volatilizing, and low stability of particles in the matrix owing to particle's heavy density. In this study, an appropriate glycerin was added into the gelatin/water admixture matrix to improve the stability, and nonwater soluble starch particles, a crude organic macromolecule with light density, were used to replace barium titanate particles to improve particle's dispersion. The aim is to produce water-based, crude organic ER elastomers, a sort of potential bionic intelligent material, which will be innocuous, friendly, and cost less.



Figure 1 Scanning electron microscopy of starch particle.

#### **EXPERIMENTAL**

#### Materials

Gelatin (B.R.  $\overline{M}_w = 77,970$ ,  $\overline{M}_w/\overline{M}_n = 1.16$ ), was bought from the Third Chemical Factory of Tianjin, China. Glycerin (98%) and formaldehyde solution (A.R. 40%, diluted to 4% when used) were from the Chemical Factory of Xi'an, China. Nonwater soluble corn starch  $\overline{M}_w = 1.28 \times 10^6$ ,  $\overline{M}_w/\overline{M}_n = 15.14$ ) was from the Starch Factory of Xi'an, China. Its density is 1.5213 g/cm<sup>3</sup> and its particle size is about 6–12 µm, and mostly about 8–10 µm, which is confirmed by scanning electron microscopy (SEM) in Figure 1. Barium titanate was synthesized in our laboratory,<sup>13</sup> and its density is 3.5984 g/cm<sup>3</sup>. Deionized water was used in all procedures.

#### Sample preparation

A 30% gelatin of aqueous solution was prepared at 60–70°C, and then added an appropriate glycerin. The specific amounts of starch particles, with weight fractions of 0, 5, 10, 15, 20, and 25%, respectively, were dispersed in gelatin/glycerin/water solution with grinding, in an agate mortar at 70°C. After 30 min, each mixture was transferred into the custom-made casting cell (Fig. 2) and cured with a parallel dc field (2 kV/ mm) for an hour. For curing, the temperature was retained at 70°C for 30 min and then naturally cooled down to 25°C. The temperature at which the dc field was carried out was about 70-25°C. Under the temperature of 25°C, the composite physical gel was obtained after 8 h and then dipped into the chemical crosslinking agent (formaldehyde solution, 4%). After 16 h, a chemically crosslinked gel, A-elastomer, was obtained. The elastomer, B-elastomer, was prepared in the absence of an applied electric field, which the chemical composition was the same as the object elastomer. The mechanisms of the gel chemical crosslinking accounting for the action of formaldehyde is described as follows

$$\begin{split} R - NH_2 + H_2N - R + HCHO \\ & \rightarrow R - NH - CH_2HN - R + H_2O \end{split}$$

The barium titanate/gelatin water-based elastomer was prepared by the reported method.<sup>13</sup>

#### Mechanical and electrical property measurement

Compression modulus measurement

The elastic modulus of elastomer is a primary mechanical property. It can be performed with shear stress and compression stress. In this article, we describe it with compression modulus. According to the elasticity theories, the compression modulus (E) could be explained by the following formulas:

$$E = \frac{F/A}{\Delta L/L_o} \tag{1}$$

$$A = A_o \left(\frac{L_o}{L_o - \Delta L}\right) \tag{2}$$

where *F* is the uniaxial force applied to a sample over its corresponding area *A*, *A*<sub>o</sub> is the sample's original area, *L*<sub>o</sub> is the original height of the sample, and  $\Delta L$  is the change in width of the sample induced by the externally applied force.<sup>11</sup>

The continuous static-state loading measurement was carried out with the custom-made apparatus, as shown in Figure 3. The dc electric fields (varying from 0 to 2.7 kV/mm), across a 3-mm gap with dc high-voltage generator (WYZ-010, China), were applied to the sample. The sample was compressed slightly to ensure it is in good contact with the copper electrode pieces, which were in the same area of the sample and



**Figure 2** Schematic equipment for cure an elastomer and measure its electric resistivity. A: HV power source, B: multimeter.



**Figure 3** Sketch of measure instrument for compression modulus of the elastomer. A: HV power source; B: shore; C: mm meter (0.01 mm); D: force-transmeter; E: copper electrode; F: sample; G: loads; H: platform.

wrapped with the insulate film. The force was loaded onto the transmitter of a millimeter instrument (Harbin Axletree Factory, China) and then compressed to the sample of  $20 \times 20 \times 3 \text{ mm}^3$  size, overlaid with a thin glass piece. The force was applied to the sample in the same direction of the field for curing and measurement. When the sample was compressed, the  $\Delta L$  value was displayed in the millimeter instrument. With the force continuously increasing, a series of  $\Delta L$  values were obtained. Based on the results, the stress–strain curve was drawn. From the drawing, the values of the stress and strain in elastic region were chosen and linear -fitted, following the formula  $F/A = E(\Delta L/L_0)$ . As a result, *E* of the elastomer sample was obtained. Measurements were performed at 25–30°C.

#### Electric resistivity measurement

Electric resistivities of composite systems were carried out by a multimeter in the direction of the applied field for curing, as depicted in Figure 2. The measurements were maintained for 90 min until the resistivities of the systems did not change any more.

#### **RESULTS AND DISCUSSION**

#### Mechanical properties of the starch/gelatin/ glycerin elastomers

Response to an applied electric field on compression modulus of the elastomer

The starch/gelatin/glycerin elastomer, cured in the presence of electric field (2 kV/mm), was denoted A-elastomer, and the same chemical composition elastomer cured in the absence of electric field was denoted *B-elastomer* oppositely.

Compression modulus of the elastomers was measured in the absence and presence of field, referred as

E and E', respectively. Figure 4 shows that compression modulus of both A and B-elastomers increases with the weight fraction of particles probably due to "particle's filler-effect".14 The effect increases with particle's concentration and induces the elastomers' stiffness to increase. In addition, a noticeable phenomenon is found from the figure: the modulus of A-elasto*mer* in the absence of field  $(E_A)$  is larger than that of *B-elastomer* in the presence of field  $(E'_B)$ . For a determinate chemical composition system,  $E_A$  is the result induced by the field for curing, and  $E'_B$  is induced by the field for measuring. According to the dielectric polarization theory,<sup>10,11</sup> the particles dispersed in the matrix are polarized as dipoles under an applied dc field and the attractive/repulsive interactions between dipoles make the particles aggregate as pearl chains.<sup>15</sup> The particles in *A-elastomer* align easily because they have been polarized before the matrix is cured as colloid. Consequently, the A-elastomer possesses higher modulus, whereas the particles in the *B*-elastomer have been restricted in the cured matrix before they are polarized. Hence, they are difficult to move and form particle chains under the applied field for measuring.<sup>11,16,17</sup> As a result, the *B-elastomer* possesses lower modulus. That is why  $E'_B$  is lower than  $E_A$ . This phenomenon indicates that the effect of the applied field for curing is stronger than that for measuring.

Also from Figure 4, it is found that particle concentrations at 0 and 5%, the modulus of *A*-elastomer in the presence of a field ( $E'_A$ ) is smaller than that in the absence of the field ( $E_A$ ). But  $E'_A$  is much larger than  $E_A$  when the particle concentration increases over 10%. The reason is probably because the macromolecules of the matrix are polymerized anisotropically under an applied dc electric field for curing, and the anisotropic structure of the matrix makes the stiffness of elastomer decrease under an applied field for measuring. When particles are dispersed orderly in the elastomer



**Figure 4** Compression modulus of *A* and *B*-elastomer as a function of the weight fraction of starch.



**Figure 5** Compression modulus of *A* and *B*-elastomers as a function of dc electric field strength.

the elastomer's stiffness increases. However, the stiffness increases slightly when the particle concentration  $\leq$ 5%. The small increment is not able to counteract the stiffness decrement from the anisotropic matrix, and then  $E'_A$  is still low.<sup>13,18</sup> When the particle concentration increases up to 10%, the stiffness increment, which is induced by ordered particles, strongly counteracts the stiffness decrement, and eventually  $E'_A$  is much larger than  $E_A$ . The result suggests that the elastomer has great response to the field with the particle concentration.

Influence of the applied field strength for measuring the elastomer's modulus

As the best response of the elastomer appears at 25 wt % starch, as shown in Figure 4, the modulus of A and B-elastomers with 25 wt % starch were chosen and tested under the field ranging from 0.5 to 2.0 kV/mm. The results are shown in Figure 5: (1)  $E'_A$  and  $E'_B$  are enhanced by increasing field strength, indicating the positive ER effects of A and B-elastomers; (2)  $E'_A$  does not increase anymore with increasing the field strength when the strength larger than 1.5 kV/mm. Whereas,  $E'_B$  increases continuously with increasing the field strength till 2 kV/mm. The phenomena are probably interpreted as following: the previously polarized particles in A-elastomer are polarized ulteriorly by the measuring field, and the attractive interaction increases. With an increase of the field strength, the interaction becomes stronger and induces the particles to aggregate closer in lines. Consequently, the modulus of the elastomer becomes larger. When the measuring field reaches 1.5 kV/mm, the polarization of particles rise to the top, and the interaction of particles does not increase any more with the increase of the field strength,<sup>19</sup> so  $\vec{E'}_A$  approximately remains

steady. However, for *B-elastomer*, the polarization of particle can not reach the top under 1.5–2.0 kV/mm measuring field, and then  $E'_B$  increases continuously with the increase of field strength.

Actually in experiments, the field of the application apparatus could not be applied more than 2.0 kV/mm. We will discuss the modulus increment under the field of >2.0 kV/mm in the future.

# Comparison in response to an electric field with the barium titanate/gelatin elastomer

Both barium titanate/gelatin and starch/glycerin/gelatin elastomers are gelatin–water based. The response to an applied electric field on compression modulus of the anterior elastomer was reported in Ref. 13.

It is noticed that there are a few similar phenomena for the two elastomers. One is that their compression moduli increase with increasing the applied field strength, and the other is that they both have modulus peaks with the weight fraction of particles.

Also, some differences between them are noticed. The matrix, which improved with an appropriate glycerin addition, makes the object elastomer's geometrical shape and mechanical performance steady. Figure 6 shows relative change in modulus ((E'-E)/E)of BaTiO<sub>3</sub> and starch of *A*-elastomer as a function of the weight fraction of particle. Under the measuring electric field, the BaTiO<sub>3</sub> elastomer's largest value of (E'-E)/E was 79.36% at 1.5 wt % BaTiO<sub>3</sub>. Oppositely, the starch elastomer's largest value of (E'-E)/E was only 21.04% at about 20 wt % starch. The dominating factors of this result are probably the differences in density and relative permittivity of the two particles. Low density of particle is an advantage to reduce sedimentation and is a foundation of good ER effect. The density of the BaTiO<sub>3</sub> and starch particle is 3.5984 and 1.5213 g/cm<sup>3</sup>, respectively. Sedimentation of the BaTiO<sub>3</sub> particle, due to its heavier density, induces its



**Figure 6** Relative change in modulus of BaTiO<sub>3</sub> and starch *A-elastomer* as a function of the weight fraction of particle.



**Figure 7** Electric resistivity of the systems cured in the absence/presence of dc electric field, with the weight fraction of starch particle of 0 and 5 wt %.

poor dispersion in the matrix at  $BaTiO_3 > 1.5$  wt %. Contrarily, the lower density of starch particle makes particle disperse well in the matrix, and then the weight fraction of particle extends to 25 wt %. As a result, the starch elastomer's largest response to the applied field appears at 20–25 wt % starch, and the BaTiO<sub>3</sub> elastomer's largest response only appears at 1.5 wt % BaTiO<sub>3</sub>.

Furthermore, the relative permittivity of BaTiO<sub>3</sub> is about 2000.<sup>20</sup> Whereas, the relative permittivity of the starch is about 2–5.<sup>21</sup> According to the dielectric polarization theory, the BaTiO<sub>3</sub> particles that possess higher relative permittivity are strongly polarized under an electric field. The strong interactions between the polarized particles induce strong ER response. On the other hand, starch particle possesses lower relative permittivity and is weakly polarized. The interactions between the polarized particles are weak, and there-



**Figure 8** Resistivity and resistivity increment as a function of the weight fraction of starch.



**Figure 9** Electric resistivity of BaTiO<sub>3</sub> and starch elastomers in the absence/presence of dc electric field.

fore induce weak ER response. So it was possible that the large difference in the relative permittivity induces the obvious difference in the ER response, as described in the previous paragraph.

#### The electric resistivity of the water-based systems

Electric resistivity of the starch/gelatin/ glycerin system

To compare the properties of *A* with *B*-elastomer ulteriorly, the electric resistivity of the two corresponding systems was tested in the course of cure. Figure 7 shows electric resistivity of the systems cured in the absence/presence of dc electric field, with the weight fraction of starch particle of 0 and 5 wt %. In the figure, the temperature of the systems remained at 60–70°C in section AB, and cooled down spontaneously from 70 to 25°C in section BC. The 2 kV/mm field was applied for 1 h in section AC (section AB + section BC).

In Figure 7, the two electric resistivity curves of the nonstarch system, cured in the absence and presence of the field (2 kV/mm) respectively, show similar behavior. This phenomenon indicates that the 2 kV/mm electric field for curing has little influence on non-starch system.

Also in Figure 7, for 5 wt % starch system, there is a distinct increment of electric resistivity between the system cured with the 2 kV/mm field and without the field. This is the evidence that the 5 wt % starch system has an obvious response to the applied field. It is presumed that the curing field aligns particles in the matrix and induces an additional electric resistivity in the system.

In a series of systems with weight percent of 10, 15, 20, and 25, the electric resistivity increments are similar to that of the 5 wt % one. Evidently, the electric re-

## 流变学通讯

sistivity with an applied field is larger than the one without a field. But the value of increment varies with the particle contents, as shown in Figure 8. The largest increment appears in the 25 wt % starch system. This result matches with the results shown in Figure 4—the maximum values of  $E_A$  and  $E_B$  appears at 25 wt % starch.

Comparison in the electric resistivity with barium titanate/gelatin elastomer

Figure 9 shows the electric resistivity curves of BaTiO<sub>3</sub> and starch elastomer (both weight fraction of particles are 1.5%) with and without an electric field. In the figure, the electric resistivity of BaTiO<sub>3</sub> elastomer is larger than that of starch elastomer, and its resistivity increment, influenced by the dc electric field, outclasses that of starch elastomer. This phenomenon indicates that the two elastomers have obvious difference in response to the field. Perhaps it is because the particles have the apparent difference in the relative permittivity and density, as mentioned earlier. This result matches the fact, which was described in section "Comparison with the barium titanate/gelatin elastomer," and reveals the difference in response of the two elastomers to an applied field.

#### CONCLUSIONS

The starch/gelatin/glycerin composite hydrous ER elastomers were prepared under an applied dc electric field, and a series of tests on compression modulus and electric resistivity were carried out. It is found that the mechanical and electrical properties of the elastomers are controlled by an applied electric field and the weight fraction of particles. Compared to the

elastomer cured without a field, it is found that the response to an applied field for curing is stronger than that for measuring. And compared to the barium titanate/gelatin elastomer, the results indicate that the differences of ER response of gelatin water-based elastomers are mainly induced by the difference in particle's density and relative permittivity.

#### References

- Havelka, K. O. Progress in Electrorheology; Plenum: New York, 1995; p 43.
- Parthasarathy, M.; Klingenberg, D. J. Mater Sci Eng 1996, R17, 57.
- 3. Zrínyi, M.; Fehér, J.; Filipcsei, G. Macromolecules 2000, 33, 5751.
- 4. Zhao, Q.; Zhao, X. P.; Qu, C. Z.; Xiang, L. Q. Appl Phys Lett 2004, 84 1985.
- 5. Kanu, R. C.; Shaw, M. T. J Rheol 1998, 42, 657.
- Bohon, K.; Krause, S. J Polym Sci Part B: Polym Phys 1998, 36, 1091.
- Zhao, X. P.; Liu, S.; Tang, H.; Yin, J. B.; Luo, C. R. J Intell Mater Syst Struct 2005, 16, 57.
- 8. Shiga, T.; Okada, A.; Kurauchi, T. Macromolecules 1993, 26, 6958.
- An, Y. X.; Liu, B.; Montgomery, T. S. Int J Mod Phys B 2002, 16– 18, 2433.
- 10. Liu, B.; Shaw, M. T. J Rheol 2001, 45, 641.
- 11. Krause, S.; Bohon, K. Macromolecules 2001, 34, 7179.
- Nichols, M. E.; Ginder, J. M.; Elie, L. D.; Pett, R. A.U.S. Pat. 5,607,996 (1997).
- 13. Gao, L. X.; Zhao, X. P. J Appl Polym Sci 2004, 94, 2517.
- Botti, A.; Pyckhout-Hintzen, W.; Richter, D.; Straube, E. Phys A 2002, 304, 230.
- 15. Hanaoka, R.; Takata, S.; Nakazawa, Y.; Fukami, T.; Sakurai, K. Electr Eng Jpn 2003, 142, 1.
- 16. Zhao, H. P.; Liu, Z. Y.; Liu, Y. Y. Phys B 2001, 299, 64.
- 17. Wang, B.; Liu, Y. L.; Xiao, Z. M. Int J Eng Sci 2001, 39, 453.
- 18. Mitsumata, T.; Sugitani, K.; Koyama, K. Polymer 2004, 45, 3811.
- 19. Block, H.; Kelly, J. P. J Phys D: Appl Phys 1988, 21, 1661.
- 20. Park, C.; Robertson, R. E. Mater Sci Eng A 1998, 257, 295.
- 21. Ndife, M. K.; Sumnu, G.; Bayindirli, L. Food Res Int 1998, 31, 43.

## Gelling properties of waxy crude under quiescent and shearing conditions

LI Hong-ying(李鸿英)<sup>1</sup>, ZHANG Jin-jun(张劲军)<sup>1</sup>, CHEN Jun(陈 俊)<sup>1,2</sup>, SUN Li-xin(孙立新)<sup>1</sup>

(1. Beijing Key Laboratory of Urban Oil and Gas Distribution Technology,

China University of Petroleum(Beijing), Beijing 102249, China; 2. Beijing Huayou Natural Gas Co. Ltd, Beijing 100101, China)

Abstract: Gel point or pour point is the temperature indicating the gelling of waxy crude, and is widely used for evaluating the low temperature flowability of a crude oil. While they are not sufficient to describe the gelling properties of waxy crudes under flow conditions, since the rheological properties of waxy crudes are strongly dependent on shear history. The gelling characteristics of waxy crude were investigated by dynamic temperature sweep measurements. At a given dynamic stress, the gelation temperature at which the storage modulus equals the loss modulus almost coincides with the eigen-temperature, the temperature corresponding to the maximum value of the curvature of a non-dimensional viscosity-temperature chart. For the rather low stress, the wax crystal network formation will not be disturbed, and the crude is gelled as under the quiescent conditions, both gelation temperature and eigen-temperature are close to the gel point of the specimen. However, they decrease with the increasing shear stress. This suggests that these two parameters may be appropriate measures of the onset of gelling under static as well as flow conditions.

Key words: waxy crude; gelation temperature; eigen-temperature; gelling characteristic; viscoelastic property

#### **1** Introduction

Waxy crudes, which contain significant quantities of wax, are known to form a gel-like structure when the crudes are cooled below certain temperature. Gel point and pour point are widely used as industrial standard to indicate the gelling of waxy crude. Gel point is the highest temperature at which movement of the specimen cannot be observed under the conditions of test. While pour point is the lowest temperature at which movement of the test specimen is observed under the conditions of test. Since these two parameters are tested under the quiescent conditions, they are not sufficient to describe the gelling properties of waxy crudes under flow conditions because the rheological properties of waxy crudes are strongly dependent on shear and thermal history<sup>[1-2]</sup>.

Gelling process of waxy crudes can be evaluated by viscoelastic parameters. SINGH et al<sup>[3]</sup> studied the gelation process of wax-oil system by a universal stress rheometer RS75, and defined the temperature at which the loss modulus equals the storage modulus as the gelation temperature. LI et al<sup>[4]</sup> showed that the gelation temperature, which obtained in small amplitude oscillatory shear temperature sweep experiments, coincides with the gel point determined by standard test method if the temperature sweep is made at cooling rates

of 0.5–1.0 °C/min. The previous study was carried out by small amplitude oscillatory shear, which has the advantage of continuously observing evolution of the viscoelastic properties without destroying the wax crystal structure of the specimen. However, waxy crudes experience extensive shearing during pipelining, which inevitably disturbs the formation of wax crystal network, thus the crude gelling process is quite different from that under the quiescent conditions. In this study, the gelling characteristics of waxy crude under dynamic shear conditions were investigated by the viscoelastic experimental results.

#### 2 Experimental

Two typical waxy crudes from East China were used, their main properties are listed in Table 1.

Table 1 Properties of crude samples					
Sample	$ ho_{20}$	Wax content	WAT	Gel point	
	/(kg·m <sup>-3</sup> )	/%	/°C	/℃	
А	858	25.4	43.2	32	
В	849	20.2	49.7	33	

A controlled-stress rheometer RS150 was used to study the gelling properties of waxy crude. The experiment started with heating the oil specimen to the

Foundation item: Project (04E7019) supported by the Youth Innovation Fund of China National Petroleum Corporation Corresponding author: ZHANG Jin-jun, Professor; Tel: +86-10-89734627; E-mail: zhangjj@cup.edu.cn

preheating temperature, and then loading the specimen into the coaxial cylinder system preheated to the same temperature. Dynamic temperature sweep measurements were performed with different shear stress amplitudes at a cooling rate of 0.5 °C/min and a frequency of 1 Hz.

#### **3** Results and discussion

A representative plot of the viscoelastic data of waxy crudes is shown in Fig.1. The storage modulus G', the loss modulus G", and the complex viscosity  $\eta^*$ , are plotted as a function of temperature. At temperatures higher than the wax appearance temperature (WAT), all wax is dissolved in liquid oil,  $\eta^*$  and G" increase slowly with temperature decreasing. While the value of G' is rather low and almost remains unchanged, and G'' is an order of magnitude higher than G', indicating that the crude oil behaves as an inelastic fluid. At the temperature of WAT, wax particles start to precipitate. This leads to the loss modulus and viscosity of the oil increase somewhat speedily, however, G' still remains unchanged. With further decreasing of temperature, the precipitated wax particles start to interact with each other and tend to form a network. As a result, the viscosity of the crude increases more rapidly, in the meantime, sharp increases in the viscoelastic modules are observed. As temperature lowers further, interaction among the wax particles increases rapidly. So both viscosity and the shear module increase further, while G' increases more rapidly as compared to G''. This causes G' and G'' vs temperature curves approach each other and intersect at a certain temperature. Then it can be observed that G' > G'', indicating a gel formation is established.



Fig.1 Curves of viscoelastic parameters vs temperature of sample A (stress amplitude: 1 Pa, heating temperature: 45 °C, cooling rate: 0.5 °C/min)

#### 3.1 Gelation temperature

The common definition gelation temperature is the temperature at which the storage modulus equals the loss modulus. G'-G'' crossover is used and considered

satisfactory to indicate the sol-gel transition in many studies, especially for some fast aggregation process.

The gelation temperatures at different dynamic stresses are shown in Table 2. A decrease in gelation temperature was observed with increasing of the dynamic stress. The gelation temperature obtained at the lowest stress (0.1 Pa) almost coincides with the gel point of the specimen. Since such low stress cannot efficiently disturb the wax crystal network formation, the crude sample is gelled under quiescent conditions. With the increasing of the forced dynamic stress, the aptitude to destroy the wax crystal structure increases, this makes the wax crystal network will not be formed until more wax particles precipitate, thus the gelling of the crude is delayed and the gelation temperature under shear condition is lower than that under quiescent conditions.

Sample	Stress amplitude /Pa	G'=G" /Pa	Gelation temperature /°C	Eigen temperature /°C
	0.1	6.10	32.5	31.8
	1.0	0.21	20.0	20.0

Table 2 Comparison between gelation and eigen-temperature

Sample	ampillude	/Pa	temperature	temperature
	/Pa		/°C	/°C
A	0.1	6.10	32.5	31.8
	1.0	8.31	30.9	29.0
	4.0	15.84	29.1	28.6
	7.0	25.23	27.9	28.2
	10.0	29.91	27.3	26.8
В	0.1	3.82	33.4	31.7
	1.0	6.01	32.0	30.9
	4.0	11.25	29.8	29.4
	7.0	16.20	29.0	28.7
	10.0	21.59	28.1	28.0

#### 3.2 Eigen-temperature

Our study has shown that an eigen-temperature can be obtained from the viscosity-temperature sweep experiment. The eigen-temperature was found and put forward according to the results of viscosity and temperature sweep experiments under the steady shear condition<sup>[5]</sup>. The eigen-temperature is the temperature corresponding to the maximum value of the curvature of a non-dimensional viscosity-temperature chart.

It is found fortunately that the tendency of complex viscosity along with temperature in dynamic tests is very similar to that of the viscosity temperature curve obtained under steady shear conditions. That is, the complex viscosity increases slowly with temperature decreasing when the specimen temperature is higher than WAT or just below WAT, then viscosity increases rather rapidly with the decreasing of the temperature, when the temperature is cooled to a certain temperature, the viscosity increase rate slows down.

According to the method put forward in Ref.[5], the eigen-temperatures were obtained from the complex viscosity and temperature data at different dynamic

stresses. The eigen-temperatures also decrease with increasing of the dynamic stress, this tendency is similar to that of gelation temperature, as seen in Table 2.

# 3.3 Correlation between gelation temperature and eigen-temperature

From Table 2, it can be seen that the gelation temperature almost coincides with the eigen-temperature at a given dynamic stress, while the eigen-temperatures are somewhat a little lower than the corresponding gelation temperature.

## **4** Conclusions

1) The gelling chrematistics of waxy crude were investigated by dynamic temperature sweep measurements. A decrease in both gelation temperature and eigen-temperature were observed with increasing the dynamic stress.

2) The gelation temperature is the temperature at which the storage modulus equals the loss modulus, while the eigen-temperature is the temperature corresponding to the maximum value of the curvature of a non-dimensional viscosity-temperature chart. The gelation temperature stands for the transition from liquid to gel, while the eigen-temperature is the turning point of rheological properties of the specimen. At a given dynamic stress, the gelation temperature almost coincides with the eigen-temperature.

3) For the rather low stress, the wax crystal network formation will not be disturbed, and the crude is gelled under quiescent conditions, both gelation temperature and eigen-temperature are close to the gel point of the specimen. However, they decrease with the increasing shear stress. This suggests that these two parameters may be appropriate measures of the onset of gelling under static as well as flow conditions.

## References

- WARDHAUGH L T, BOGER D V. Flow characteristics of waxy crude oils: Application to pipeline design[J]. AIChE Journal, 1991, 37(6): 871-885.
- [2] RØNNINGSEN H P. Rheological behavior of gelled, waxy North Sea crude oils[J]. J Petrol Sci Eng, 1992(7): 177–213.
- [3] SINGH P, FOGLER H S. Prediction of the wax content of the incipient wax-oil gel in a pipeline: An application of the controlled-stress rheometer[J]. Journal of Rheology, 1999, 43(6): 1437–1459.
- [4] LI Hong-ying, SUN Ji-shu, ZHANG Fan, et al. Determining gel point of waxy crude by small amplitude oscillatory shear temperature sweep experiment[C]// Proc XIVth Int Congr on Rheology, Korea: Seoul, 2004.
- [5] CHEN Jun, ZHANG Jin-jun, LI Hong-ying. A study on low-temperature flowability characteristic of waxy crude[C]// Proceedings of the 4th Pacific Rim Conference on Rheology. Shanghai, 2005.

## 文摘

## 表面处理对玻璃微珠/端羟基聚丁二烯悬浮体系流变行为的影响

#### 崔 伟,赵瑾朝,王承哲,周兴平,解孝林

华中科技大学化学与化工学院,材料化学与服役失效湖北省重点实验室, 湖北武汉珞瑜路 1037 号 430074

**摘 要:**分别采用 γ-环氧丙氧基丙基三甲氧基硅烷 (GPTES) 和 γ-甲基丙烯酰氧基丙基三甲氧基硅烷 (MPTMS) 偶联剂对玻璃微珠(GB)进行了表面改性,利用 Brookfield R/S 旋转流变仪测定了 GB/端羟基聚丁二烯 (HTPB) 悬浮体系的稳态粘度和屈服应力,讨论了表面改性对 GB/HTPB 悬浮体系流变 行为的影响。研究表明,未处理 GB/HTPB 悬浮体系的粘度随 GB 体积分数的增加而增大,并且两者 间的变化关系具有剪切速率依赖性。当剪切速率较低时,体系粘度随 GB 体积分数的增加而急剧增大。 偶联剂 MPTMS 改性 GB 粒子导致 GB/HTPB 悬浮体系的表观粘度发生复杂的变化,当 MPTMS 的用 量为 0.3 g/ (g GB)时,体系的粘度具有最低值。同时,MPTMS 改性 GB 粒子使 GB/HTPB 悬浮体系屈 服应力增大,当 MPTMS 用量为 0.1 g/ (g GB)时,体系的屈服应力具有最大值。且 GPTES 改性 GB/HTPB 悬浮体系更低的表观粘度值和弱的剪切变稀行为。

关键词: 悬浮体系; 偶联剂; 稳态剪切粘度; 屈服应力

## 原油流变学研究的若干进展

#### 张劲军,柳歆

中国石油大学(北京),城市油气输配技术北京市重点实验室,北京市昌平区 102249

**摘 要:**原油大体上可根据流动特性分为流动性好的轻质低凝低粘原油和流动性差的易凝高粘原油(含蜡 原油与稠油)。在析蜡点温度以下,含蜡原油表现出假塑性、触变性、屈服应力、粘弹性等丰富的非牛顿流 体流变性质,而且这些性质还有较强的剪切历史和热历史依赖性。我国易凝高粘原油产量占原油总产量的 90%以上,原油流变性质是输油管道科学设计和安全经济运行的基础数据。近10年来,由于石油工业发展 的需要,原油流变学研究在国内外越来越受到重视,产生了一批重要成果,从以往比较单纯的流变性实验 测定,经过热历史和剪切历史影响的定量实验模拟,发展到探索建立原油流变性质与热历史和剪切历史的 定量关系。目前,定量研究原油宏观流变性与蜡晶形态、结构及原油组成间的关系已成为新的研究重点和 发展趋势。本文主要总结了作者课题组近10年来在原油流变学及其应用领域的研究进展,探讨了进一步发 展的方向。

原油在管道输送过程中经历的热历史和剪切历史各异,不同原油的热历史和剪切历史效应也不相同。 研究提出了以粘性流动熵产或粘性流动能量耗散作为剪切作用的模拟量,提出了管道输送主要流动过程(管 内湍流、通过离心泵及节流阀的流动等)以及模拟装置中剪切作用的计算方法,成功实现了原油管道输送 剪切和热历史效应在理论指导下的定量实验模拟,并通过了大量实践检验。 在原油流变性计算模型和有关定量关系方面,建立了含蜡原油表观粘度与剪切速率、温度及析蜡量关 系的数学模型(即粘温关系的机理模型);建立经验模型实现了输油管道常见范围内大庆原油凝点与加热温 度和动冷终温关系的模型化描述以及表观粘度的准确预测,为输油管道水力模拟提供了完整的流变参数计 算模型;针对降凝剂改性原油,建立了剪切作用对凝点、粘度影响的经验模型;利用大量实验数据,全面 评价了现有的混合原油凝点、粘度计算模型,为工程应用提供了明确结论,并提出了便于工程应用的快速 近似计算方法,丰富了原油流动性分析计算的方法体系。

在析蜡点温度以下, 蜡晶的形态、结构以及原油的组成是影响含蜡原油宏观流变性的主要内因。定量 研究宏观流变性与蜡晶形态、结构及原油组成间的关系, 对于深化对原油流变性机理的认识、发展原油管 道输送技术都具有重要意义。利用分形与体视学理论提出了基于显微图像分析的蜡晶形态及结构的直接分 形表征方法, 实现了对蜡晶形态与结构的独立量化表征; 在此基础上,应用聚类分析法,从反映蜡晶形态、 结构及原油组成的13个特征参数中,选出了5个能有效准确表征对原油流变性产生明显影响的微观结构及 原油组成的代表性参数; 定量探讨了凝点、表观粘度、粘弹性模量、屈服应力等与蜡晶结构及原油组成特 征量的关系。此外, 在含蜡原油粘弹性、屈服特性、触变性等方面也进行了一系列研究,取得了

若干新的认识。

近年来,原油流变学应用最成功的例子是我国西部原油管道工程。该管道全长1837km,是目前我国 输油工艺最复杂的长距离原油管道。把原油流变学及改性输送研究成果应用于该管道的设计,节省了4座 加热站的建设投资逾亿元,在恶劣条件下实现了安全运行。

石油工业的需求将进一步推动原油流变学的发展。定量研究流变性与原油组成及微观结构的关系在 流变学机理研究中将受到更多的关注; 胶凝原油的粘弹性、屈服特性和触变性将吸引更多的流变学工作者, 而原油流变性质的各种计算模型、含蜡原油管道再启动过程非稳态非牛顿流动则是管道工程师们更关心的 问题,而最需要也最困难的当属从根本上改善原油的低温流动性。

关键词: 含蜡原油; 流变学; 进展; 展望

**作者简介:** 张劲军,男,博士,教授,主要研究方向为原油流变学与管道输送工艺,Tel:+86-010-89734627, Emial: zhangjj@cup.edu.cn。

## 工程聚合物热流变效应与温度场研究

李之达<sup>1,2</sup>,王花平<sup>2</sup>,黄婧<sup>2</sup>

1 华中科技大学, 力学系, 武汉 430073

## 2 武汉理工大学, 交通学院, 武汉 430063

**摘** 要:本文对缺陷演化过程中缺陷温度场的形成和演化规律、热耗散进行了实验研究。在此基础上,对 缺陷演化过程中缺陷温度场的形成和演化规律,缺陷间相互作用进行了探讨。结果表明,缺陷演化过程是 一个能量耗散过程,由于热耗散所形成的缺陷温度场具有分形特性,其分形维数不仅与缺陷间相互作用有关,而且还与时间相关,体现了缺陷演化过程跨越不同层次以及过程中层次间的协同作用效应。最后,对 ABS 材料温度场进行了数值模拟,计算结果表明: ABS 的形变热效应所致的局部温升是明显的,且塑性 区形状和内热热源密度对温度场有较大影响。

关键词:温度场;热耗散;塑性区;数值模拟

### 圆盘型腔充模过程流变解析模型与 moldflow 数值模拟结果的分析对比

## 刘跃军, 李祥刚, 黄宇刚,魏珊珊,曾广胜

湖南工业大学包装新材料与技术重点实验室,湖南株洲河西泰山路 88 号 412008 摘 要:研究了稳态下金属粉末注射填充圆盘形型腔的数学模型;对稳态下的模型进行改进,得到了振动 力场下填充型腔的数学模型。根据稳态下填充圆盘型腔的数学模型可以得到填充时间、速度分布和压力分 布。对金属粉末注射成形的充模过程用流变学解析模型和 Moldflow 软件数值模拟两种方法进行了分析, 并对两种方法的分析结果进行了对比。通过对比发现,计算浇口压力随时间的变化时,温度的影响不可以 忽略;而计算其它结果时,温度的影响可以忽略。上述结果对稳态和振动力场下的充模数学模型的改进都 有指导意义。

关键词:数学模型; Moldflow; 振动力场; PIM; 充模过程

## 石油天然气增产改造过程中流变学探讨

#### 卢拥军,梁 冲,胥 云,陈彦东

中国石油勘探开发研究院廊坊分院压裂酸化中心,河北廊坊44信箱,065007

**摘 要:**石油天然气是一种重要资源,更是国家的战略物资。提高油气藏动用程度,增加单井产量,延长 增产有效期,是石油天然气开采的重要战略。压裂和酸化是油气藏增产的主要措施,中国年施工井数达到 10000 井次以上,成为全球油气藏增产措施大国。压裂酸化是流变学在工程应用的典型实例。利用流变学 基本原理,将流变学与工程应用相结合,在油气藏压裂酸化中具有十分重要的意义。

低渗透油气藏具有复杂细小的孔喉结构、低孔隙度、低渗透率、启动压力高、低丰度、低产量特点。 该类油气藏的开发需要通过压裂和酸化等工艺方法,借助人为外界压力压开地层,形成支撑裂缝或酸蚀裂 缝,提高储层油气导流能力,增加油气产量和延长产量稳产期。压裂酸化增产稳产的主控因素包括:储层 岩石力学特征、具有粘弹性的压裂液流变性质、外界注入压力与流速、酸岩反应动力学、压裂液与酸液对 储层的损害与保护。

增产改造过程中的力学特征、化学反应和流变学行为表现在:①水马力造缝行为;②聚合物在水溶液 和酸液介质的分散、溶解、增粘与交联行为;③复杂流体在管流和缝流的流动行为与摩阻特性;④不同温、 压条件下压裂液滤失与破胶行为;⑤固液两相压裂液携砂流动与铺置行为;⑥非牛顿酸液的酸岩反应与酸 蚀裂缝特征;⑦流体表/界面化学特征与返排行为。

低渗透油气田改造的石油工程流变学的发展方向是压裂酸化材料与流体流变学、深层岩石起裂与延伸流变学和压裂酸化工程应用流变学研究。

关键词: 压裂; 压裂液; 酸压; 酸液; 低渗透; 石油; 流变学

## 岩石剪切(Ⅱ型)裂纹扩展的温度影响

#### 饶秋华,谢海峰,谢 强

中南大学 土木建筑学院,湖南长沙麓山南路 932 号 410083

**摘 要:**在深部开采、地热利用、核废料处理等工程中,裂隙岩体不仅承受拉抻、剪切或压剪荷载,而且 还承受高温高压作用,温度对岩石的力学性能及断裂特性影响较大。研究高温条件下的岩石断裂特别是亚 临界裂纹扩展对岩体工程的安全评估、灾害预测与控制等具有重要的意义。目前,国内外关于岩石断裂的 温度效应主要集中于岩石的拉伸(I型)断裂,岩石的高温剪切(II型)断裂研究较少,尚未涉及到岩石剪 切(II型)裂纹扩展研究。本文采用实验与计算的方法研究高温下岩石剪切断裂特征及裂纹扩展规律,以 寻求高温下岩石的剪切断裂韧度测试方法及止裂控制方法。

通过 MSC.Marc2005 有限元软件,推导出在 20℃、40℃、60℃、80℃、100℃不同温度下红砂岩的剪 切应力强度因子。计算结果表明:随着温度增加,裂纹尖端的应力场逐渐释放,剪切应力强度因子随之减 小。

利用剪切盒实验实现岩石的高温剪切断裂,通过自行设计的导电胶电测法实现岩石剪切裂纹扩展参数 (含裂纹起裂时刻,亚临界扩展速度及亚临界扩展时间等)的连续监测,采用扫描电镜实验观测岩石断口 的显微特征。实验结果表明:在 20℃、40℃、60℃、80℃、100℃等不同温度下,岩石试样的断裂轨迹始 终沿原裂纹面,为剪切断裂;岩石试样的裂纹尖端存在小凹坑、人字形二次裂纹等显微特征,表明岩石断 裂扩展过程中存在亚临界扩展区,亚临界扩展区长度随着温度的增加而增加。随着温度的增加,岩石的剪 切断裂韧度值增加,阻缓裂纹扩展,导致岩石的亚临界裂纹扩展时间增加、亚临界裂纹扩展速度减少。 关键词:亚临界裂纹扩展;高温;剪切(Ⅱ型)断裂;导电胶电测法;岩石

## 挑战多相复杂流体及其应用

#### 许元泽

复旦大学高分子科学系,上海邯郸路 220 号 200433

**摘** 要:现代加工工艺要求对动态过程的深入物理理解,在此复杂流体理论作为结构流变学发展的新阶段, 起着核心的作用。采用共通的多尺度物理学的方法可对一些表面不相干的对象与过程进行分析。本工作综 述用于高分子共混物加工的结构流变学本构方程,相分离法制作热塑增韧热固性树脂复合材料的形貌控制 与加工时温空间,高分子缔合与弱凝胶驱油体系多尺度流变学与驱油机理等方面的进展与面临的挑战。研 究一系列具体结论,发现多尺度的考虑才能反映事物本质,应抓住对过程起关键作用的尺度。对这三个问 题,介观很重要。各尺度相互作用间的耦合与否,往往决定模型成败。在加工模拟时必须强调在各尺度下的实验与理论的对照,从而得到深入的物理理解。

关键词:复杂流体;多尺度物理学;高分子共混物;相分离;热塑增韧复合材料;凝胶化;弱凝胶驱油体系

## 聚合物相容、相分离与复合相形态的流变分析研究

周持兴,俞炜,李润明,杨凯,周平

上海、上海交通大学流变学研究所、高分子科学与工程系, 200240

**摘 要:**针对聚甲基丙烯酸甲酯(PMMA)/苯乙烯-马来酸酐共聚物(SMA)、聚丙烯(PP)/丙烯-辛烯共 聚物(POE)、线性低密度聚乙烯(LLDPE)/乙烯-马来酸酐共聚物(EMA)/碳黑(CB)三种共混复合体 系,采用旋转流变仪动态频率扫描的实验方法测量了上述聚合物在线性粘弹性范围内的流变行为,得出了 储能模量-振动频率图、vGP 图、Col-Col 图等。这些流变曲线数据与 TEM 实验表征结果相符。研究结果 表明:(1)由动态温度扫描所得到的相分离温度明显依赖于测试所应用的频率,对所有的组成,低频测试 得到的相分离温度均低于高频测试的结果;(2)动态储能模量对相分离响应的敏感程度Ω随所施加的频率 而改变,只有当Ω大到一定的程度时相分离才能被分辨出来。通过选择合适的测试频率,流变学方法可以 得到比小角激光散射技术更小的分辨尺度。

为了消除实验中测定相转变温度明显依赖于温度扫描速度的弊病,提出了一个新的方法(DRP 方法),即联用双重蠕动模型(Double Reptation model)和 Palierne 乳液模型对动态频率扫描数据进行拟合,由此计算得出了 PMMA/SMA 和 PP/POE 的相图。与传统的光学方法和流变学方法相比,新方法可避免实验条件带来的误差,给出正确的相分离温度。

在 PMMA/SMA 相分离动态过程的检测中,流变实验给出了 0-3600 秒整个相分离过程的动态储能模量数据,而小角激光散射技术能够检测的时间局限在 600-1800 秒之间,表明流变学方法更加优越。这是因为小角激光散射法受分辨尺度的限制不能反映 NG 相分离初期的变化,受到仪器光源的限制而无法检测 NG 相分离后期的变化。

对于 LLDPE/EMA/碳黑 CB 共混复合体系的研究表明,通过流变学方法可定量地表征出炭黑在两相体 系中存在的浓度分配比,克服了采用显微技术存在的问题。

最后,我们将大分子线团流变模型、双蠕动模型和聚合物定位相互作用模型结合起来,建立了描述流 场中部分相容共混体系相行为的准平衡热力学方程。该方程将聚合物混合体系中的多尺度结构流变能量变 化与相容性定量地联系了起来,可近似地预测剪切速率对于共混体系多尺度结构流变行为与相容性的影 响,因此可以从结构演变的角度解释流场效应。

关键词:聚合物;共混复合材料;相形态;流变行为.

作者简介:周持兴,男,教授,聚合物加工流变学和共混复合材料
 Tel: 021-54743275, Email: cxzhou@sjtu.edu.cn
 基金项目:国家自然科学基金资助项目(No.50390095, No.20394004, No.20474039)

## 非线性振荡剪切用于聚合物材料结构表征的研究

俞炜,周持兴

上海交通大学流变学研究所、高分子科学与工程系, 200240 上海

**摘** 要:聚合物材料具有复杂的多尺度结构,例如聚合物分子的分子量、分子量分布以及分子链的拓扑结构、聚合物多相体系的相结构等。利用各种手段来定量表征不同尺度的结构是制备高性能聚合物材料的基本要求。聚合物材料的线性粘弹性行为可以表现出材料在平衡态的结构,利用线性粘弹性性质可以较好的表征聚合物的分子量、分子量分布和聚合物共混体系的相形态。同时,非线性粘弹性行为可以表示在非平衡状态下的结构。本文利用非线性振荡剪切流动来研究聚合物材料的结构与流变学性质之间的关系,通过 建立非线性振荡的数据分析方法,利用高次倍频的幅值与相位角来关联大分子链的拓扑结构,以及复合材料中的屈服与壁面滑移等行为。

关键词:聚合物;非线性振荡;微结构