



流变学测量技术进展及其应用

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流变产品专家

马尔文仪器（中国）

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主要内容

- › 流变学基础
- › 流变学测量原理
 - 旋转流变仪
 - 毛细管流变仪
- › 流变学应用
 - 高分子材料
 - 粉末成型
 - 电池行业
 - 公路行业
 - 食品
 - 生物医药



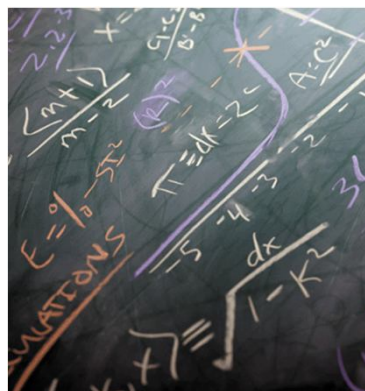
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流变学-Rheology

› 流变学是研究材料流动与变形的学科

“the science of
deformation
and flow”



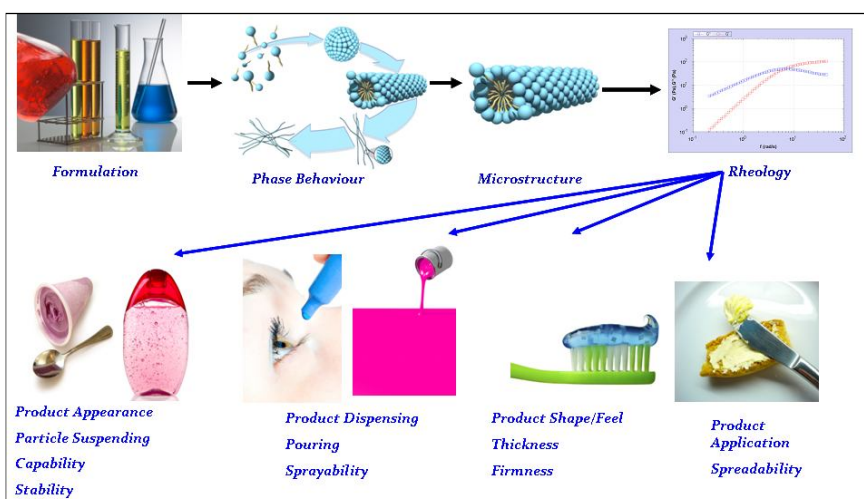
Rheology: *rheo* (to flow) + *logos* (science)



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流变学的重要性



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剪切粘度(Shear viscosity)

› 粘度就是流动的阻力

- 粘度越大，越难流动（蜂蜜，酸奶等）
- 粘度越小，越容易流动（水等）



$$\text{剪切粘度} = \frac{\text{剪切应力 (施加外力)}}{\text{剪切速率 (运动速度)}}$$

Pa.s

▶ 单位 (Unit)

- Pascal second Pa.s (SI)
- Poise P (CGS)

▶ $1 \text{ Pa.s} = 10 \text{ P}$, $1 \text{ mPa.s} = 1 \text{ cP}$



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剪切粘度(Shear viscosity)

› 粘度是...

- 剪切应力
- 剪切速率
- 温度
- 时间 (剪切历史和触变性)
- 压力 (通常是在常压下测试)

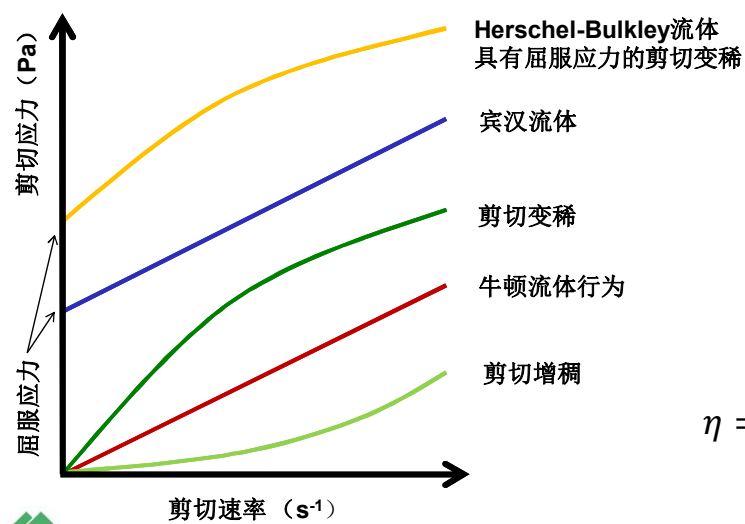
$$\eta = f(\sigma, \dot{\gamma}, T, t, p)$$



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典型的流动曲线 (Flow behavior)



$$\eta = \frac{\sigma}{\dot{\gamma}}$$

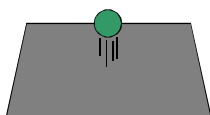
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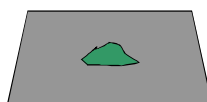
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粘弹性 – What is Viscoelasticity?

- ▶ 既具有弹性有具有粘性
 - (Combined effect of elasticity and viscosity)



Short timescale – bounce



Long timescale - flows

⇒ 弹性储存能量，粘性消耗能量
 ⇒ Elasticity stores energy, viscosity dissipates energy!



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粘弹性-Consequences of Viscoelasticity

PDMS

典型的聚合物熔体行为



短时间尺度 - 弹性主导
 长时间尺度 - 粘性主导



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粘弹性-Viscoelasticity

- › 许多材料表现出粘弹性：在某些加工过程中表现出粘性，在某些加工过程中表现出弹性
- › 材料响应依赖于观察时间尺度（**timescale**）

时间尺度
Timescale

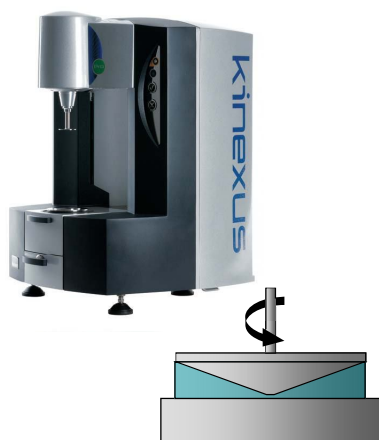


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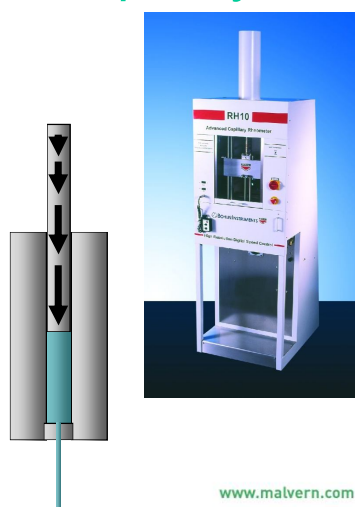
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流变学研究仪器- Rheology Instrumentation

Rotational



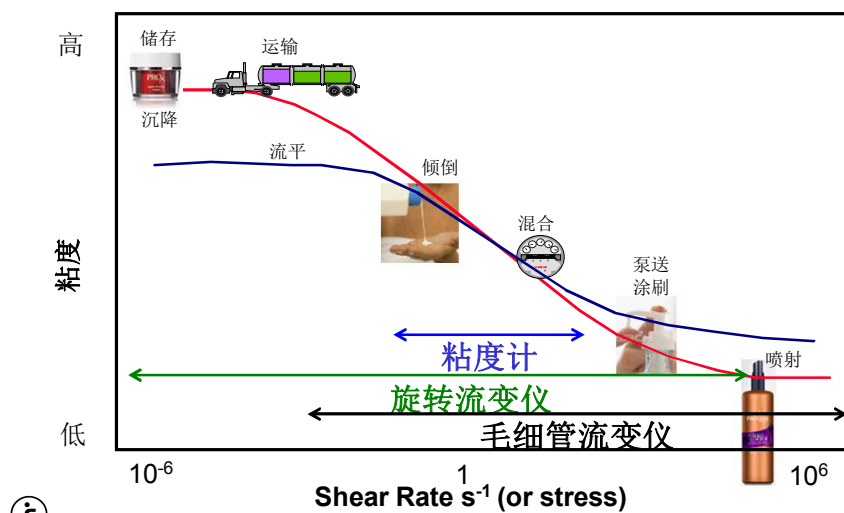
Capillary



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旋转流变仪和毛细管流变仪测试范围

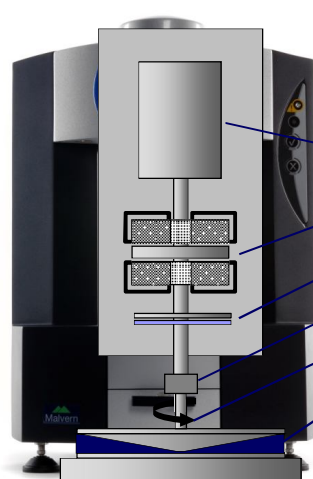


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旋转流变仪怎样工作...



› 主要部件是空气轴承组件...

› 包括:

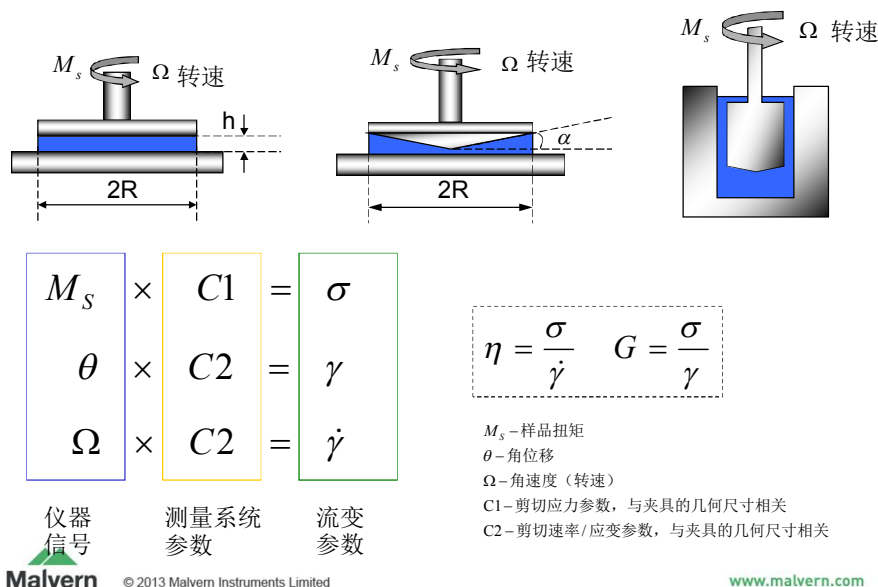
- 拖杯马达
- 空气轴承
- 位置传感器
- 保护锁
- 测量系统
- 样品

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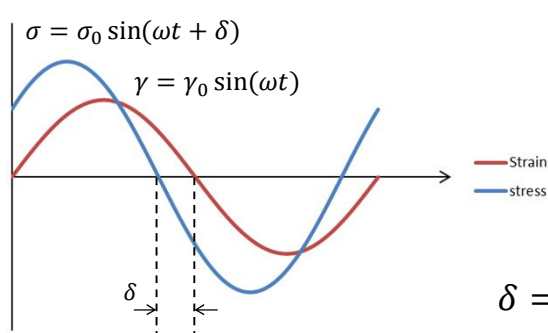
流变学测量-旋转流变测量原理



旋转流变仪应用

- › 稳态/瞬态测试
 - 流动性测试, 剪切粘度/剪切速率、时间、温度, 剪切应力, 屈服应力, 触变性等
- › 振荡测试
 - 粘弹性测试, 储能模量 (G'), 损耗模量 (G''), 损耗角 (δ), 复数粘度 (η^*), 材料结构, 固化曲线
- › 蠕变回复测试
 - 粘弹性测试, 蠕变柔量 (J), 模量, 零剪切粘度等
- › 应力松弛测试
 - 粘弹性测试, 松弛时间谱等
- › 多波测试
 - 凝胶点, 固化曲线等
- › 侧重材料内部结构

粘弹性测试 - 振荡测试 Oscillation



$$G^* = \sigma_0 / \gamma_0$$

δ 相位差

$\delta = 0$ 理想固体

$\delta = \frac{\pi}{2}$ 理想液体

$0 < \delta < \frac{\pi}{2}$ 粘弹性



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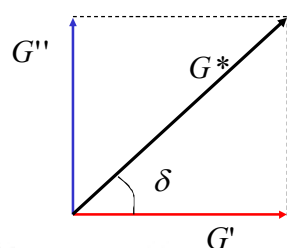
粘弹性参数

- › 复数模量 Complex Modulus (G^*) $G^* = \sigma_0 / \gamma_0$

 - 应力/应变
- › 储能模量 Storage Modulus (G') $G' = G^* \cos \delta$

 - 弹性, 可回复部分
- › 损耗模量 Loss Modulus (G'') $G'' = G^* \sin \delta$

 - 粘性, 耗散能量
- › 复数粘度 Complex Viscosity (η^*) $\eta^* = \frac{G^*}{\omega}$

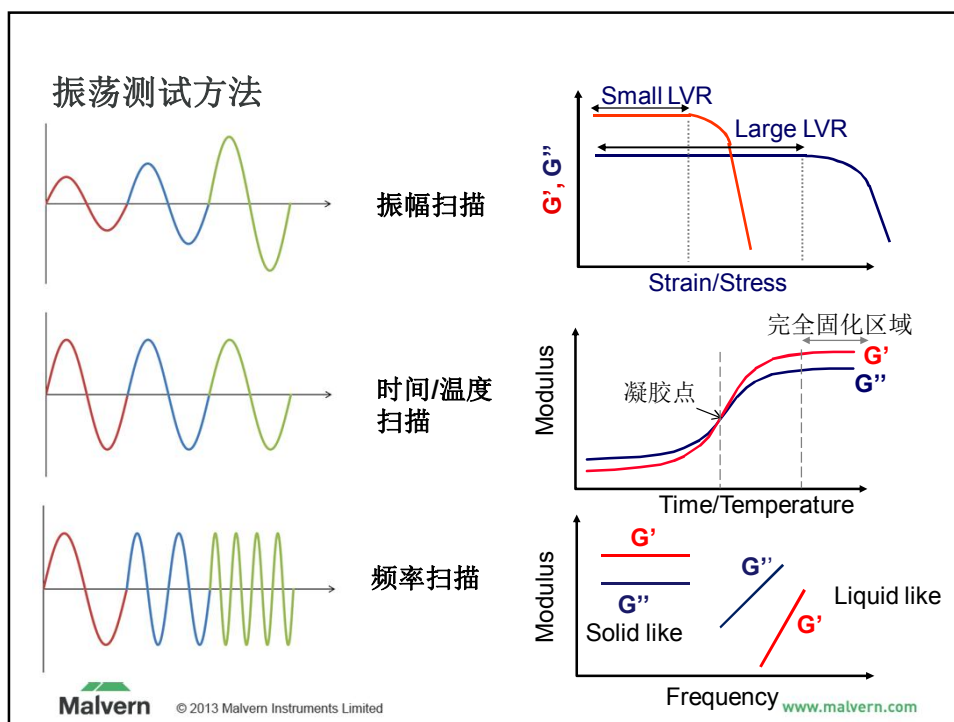


$$\tan \delta = \frac{G''}{G'}$$

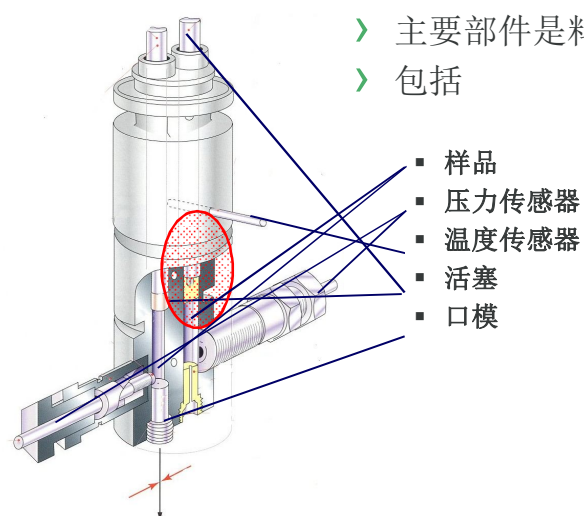


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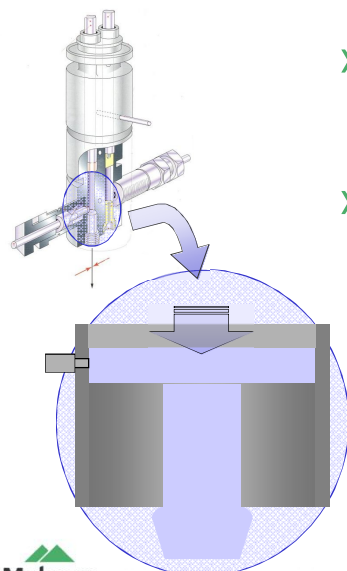
Rosand 毛细管流变仪示意图



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毛细管流变仪原理



- › 控制活塞速度(相当于控制剪切速率)
- › 压力与剪切应力相关(测量压力计算剪切应力).

$$\eta = \frac{\sigma}{\dot{\gamma}}$$



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毛细管流变仪原理

恒温, 不可压缩流体, 稳定流动

› 牛顿流体

$$\dot{\gamma}_{app} = \frac{4 \cdot Q}{\pi R^3}$$

$$\tau_{app} = \frac{R \cdot \Delta P}{2 \cdot L}$$

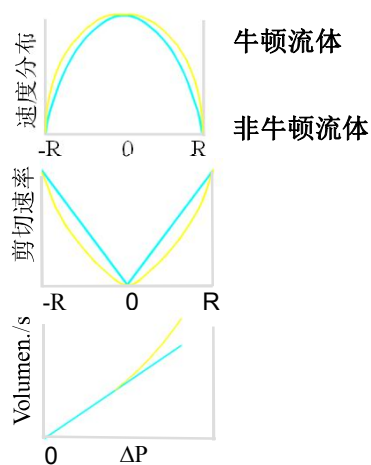
$$n = \frac{d(\log \tau)}{d(\log \dot{\gamma})}$$

校正

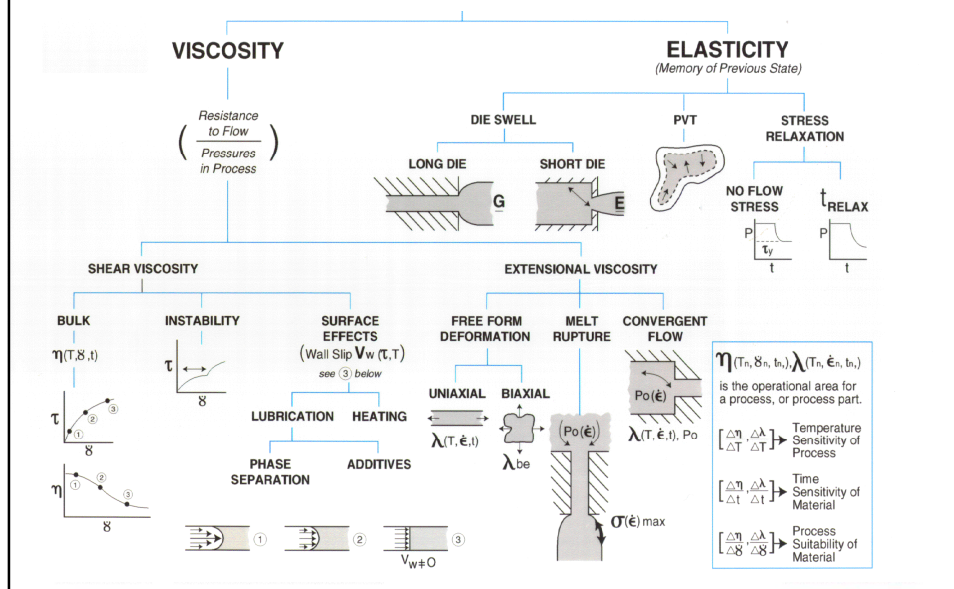
$$\eta = \frac{\tau_{True}}{\dot{\gamma}_{True}}$$



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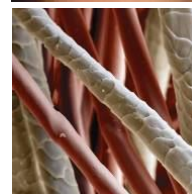


毛细管流变仪：主要应用



流变学在各行各业中的应用

- 个人护理品行业
 - 货架期、感官、屈服点、凝胶强度、脱水收缩、平滑性
- 食品
 - 质构、储存稳定性、“口感”、烹饪特性、可加工性、挤出、铺展性
- 油漆、涂料和油墨
 - 在粘辊上飞溅、雾化效果、薄膜厚度、输送、垂挂、储存时颜料沉降
- 医药品
 - 沉降、感官、屈服点、凝胶强度、脱水收缩、平滑性
- 陶瓷行业
 - 稳定性、倾倒、泵送、铸造性能
- 高分子材料
 - 注塑成型、挤出成型条件、分子量、尺寸稳定性、表面、冲击强度、玻璃化转变温度
- 粘结剂行业
 - 固化时间和凝胶点、粘接和剥离、压敏性
- 石化行业
 - 润滑剂配方、粘度-温度的关系、钻井液-携沙能力和输送性能、高温高压下的流动性能
- 公路沥青行业
 - 沥青胶料硬度、疲劳、车辙、高温和低温开裂, SHRP规范测试



高分子材料领域

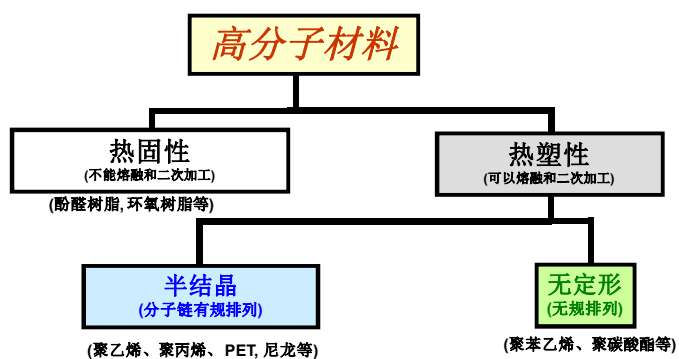


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高分子材料

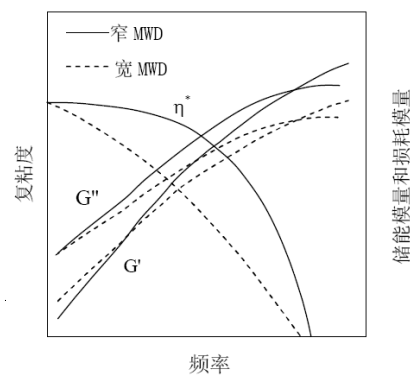
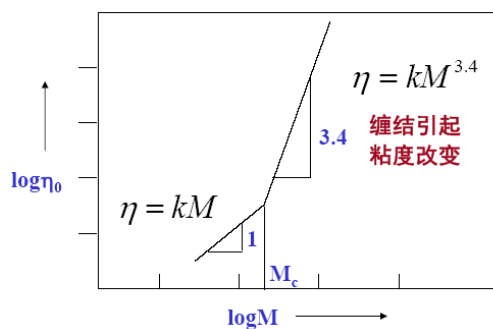
- › 现在已经有很多种合成高分子材料
- › 高分子材料必须加热熔融之后才能加工成型



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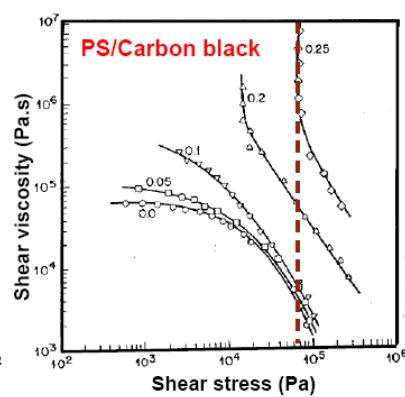
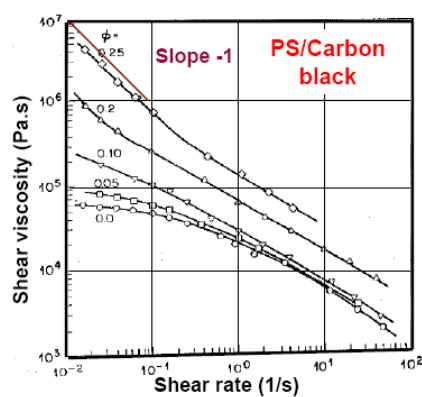
高分子材料分子结构与流变特性的关系



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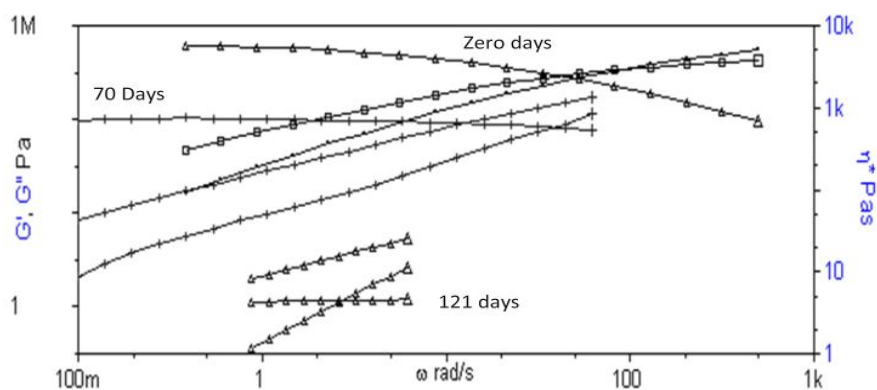
填料的体积分数对聚物流变特性的影响



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流变学方法研究聚乳酸(PLA)样品的生物可降解性

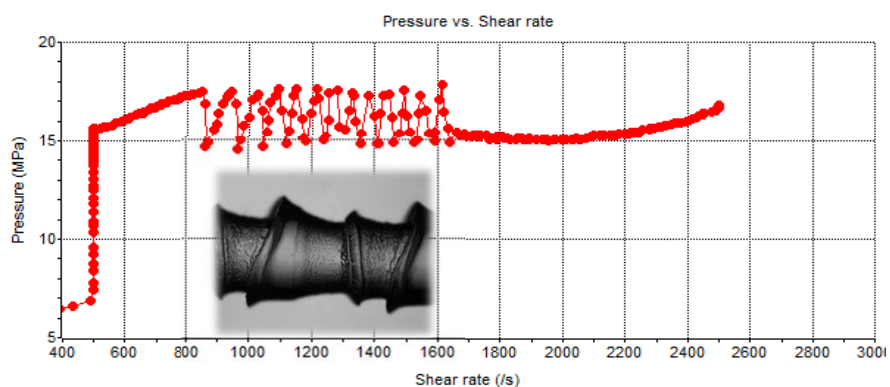


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高分子材料加工过程中的流变特性

› HDPE，熔体破裂

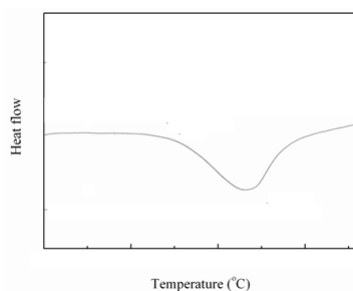


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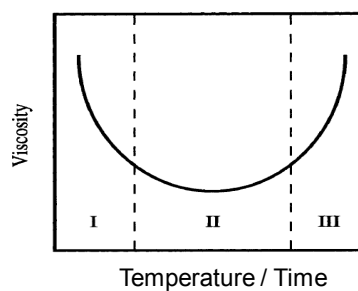
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研究环氧树脂固化过程的方法

DSC



Rheology



DSC: 反应固化的动力学过程，确定固化的起始及终止温度，反应固化活性

Rheology: 反应热运动+固化动力学的综合作用过程，确定固化的起始、终止温度，反应固化活性，同时可以确定最低粘度、加工窗口的工艺条件

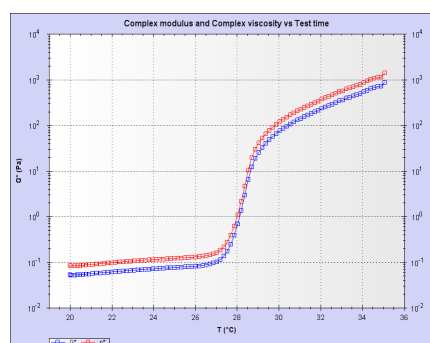
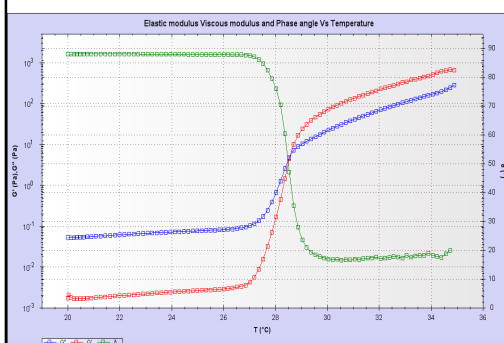
(I:热运动主导; II: 热运动及固化反应综合主导; III固化反应主导)

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凝胶点的确定 温度扫描——凝胶化温度



G' 和 G'' 的交点

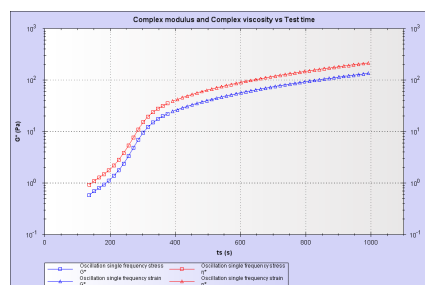
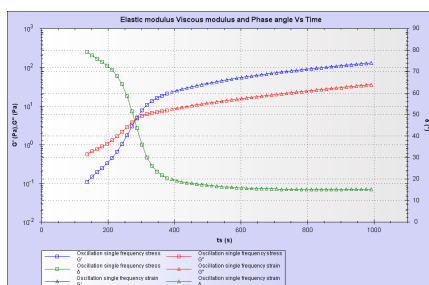
复数模量/复数粘度的拐点
复数模量和复数粘度的趋势是一致的

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时间扫描——凝胶化时间（恒温）



G'和G''的交点

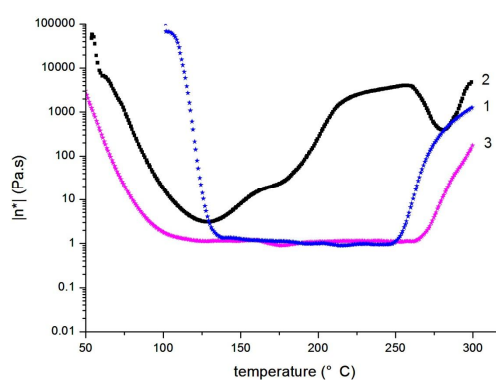
复数模量/复数粘度的拐点
复数模量和复数粘度的趋势是一致的



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环氧树脂固化的加工窗口



- 1: 改性低成本树脂
- 2: 商用高粘度树脂
- 3: 商用进口低粘度树脂（昂贵）



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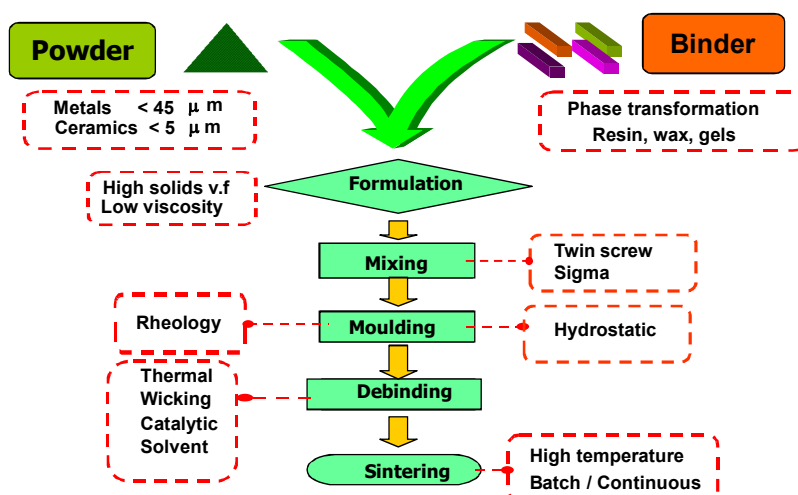
粉末成型



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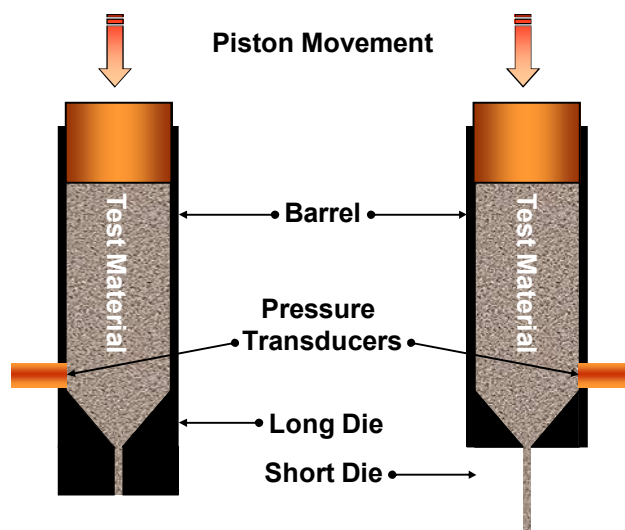
粉末注射过程



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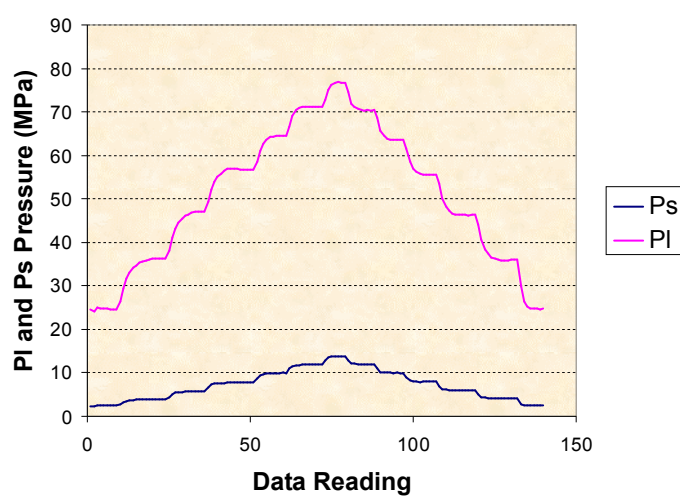
毛细管流变仪



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毛细管流变仪压力读数

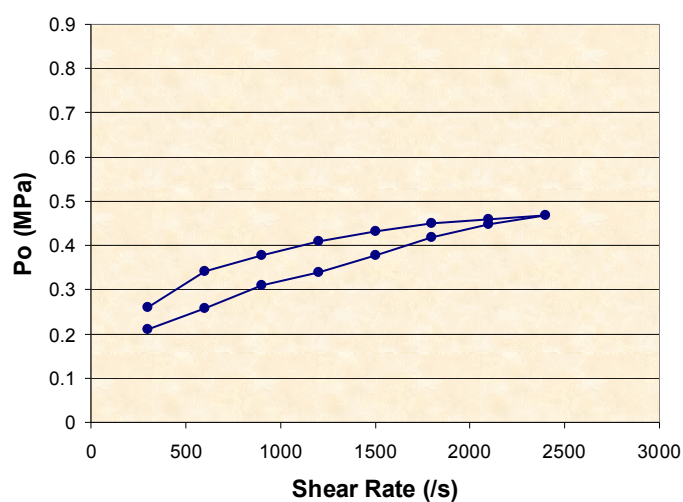


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相分离

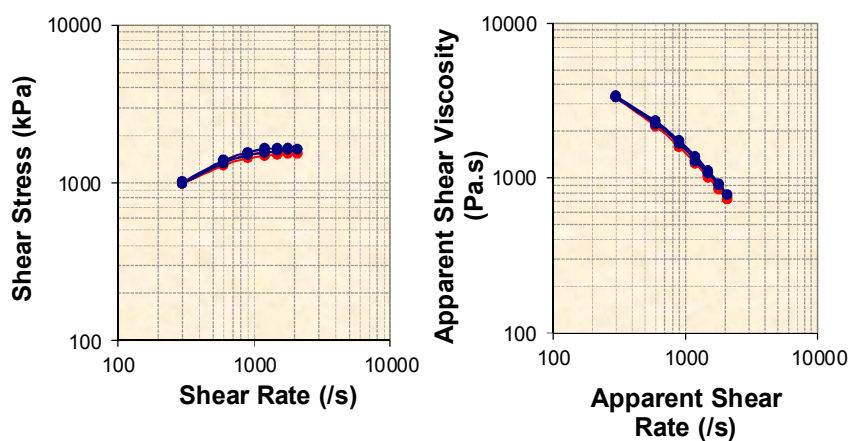


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粉末注射成型 - 混合效果

铝粉/PVA VPP 物料 剪切粘度曲线

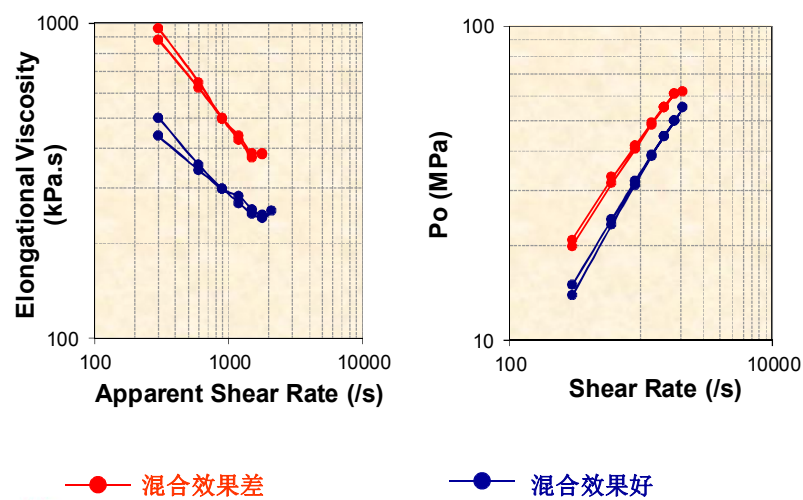


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粉末注射成型 - 混合效果

铝粉/PVA VPP 物料 拉伸粘度曲线

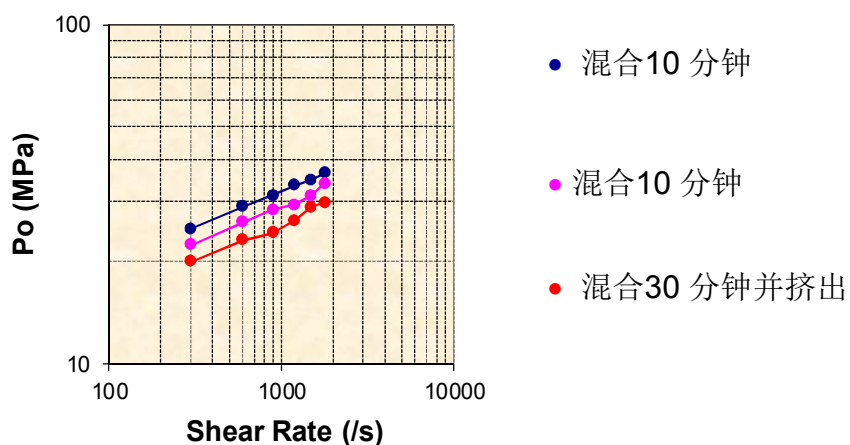


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粉末注射成型 - 混合效果

粉末注射成型物料

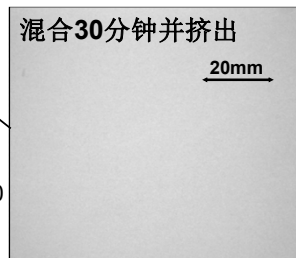
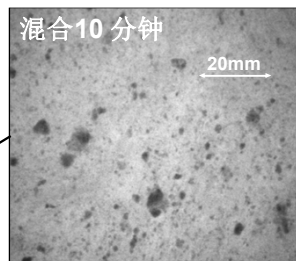
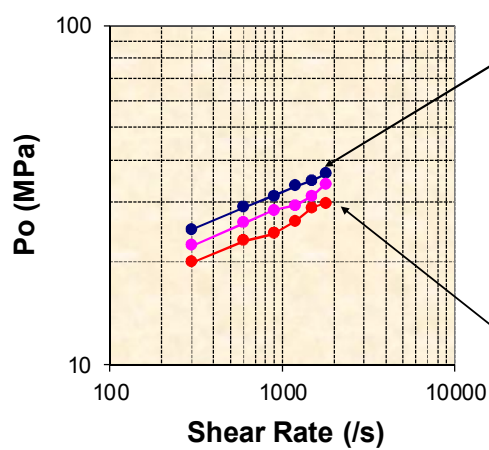


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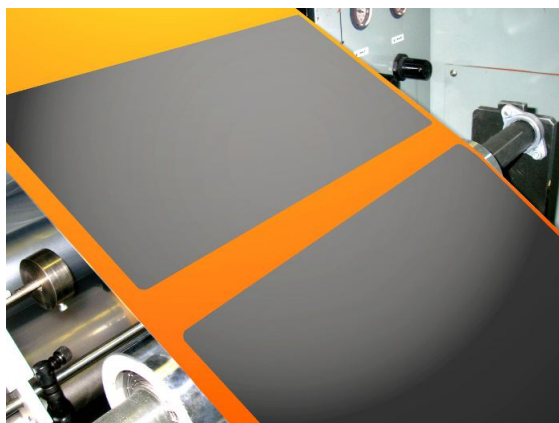
粉末注射成型 - 混合效果

粉末注射成型物料



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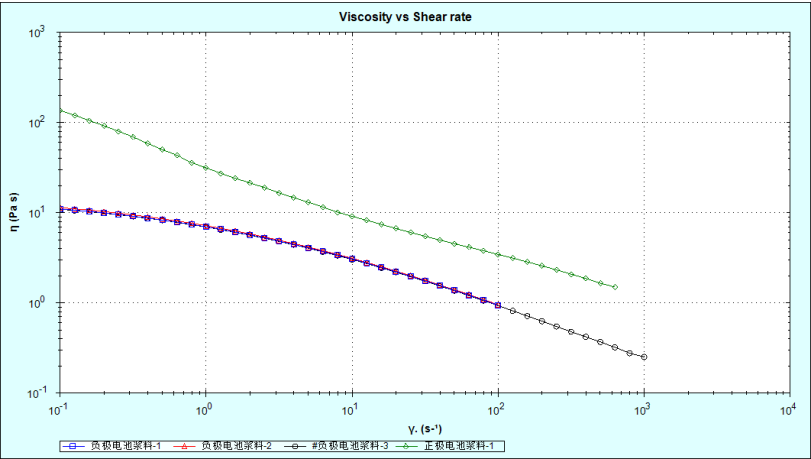
电池浆料



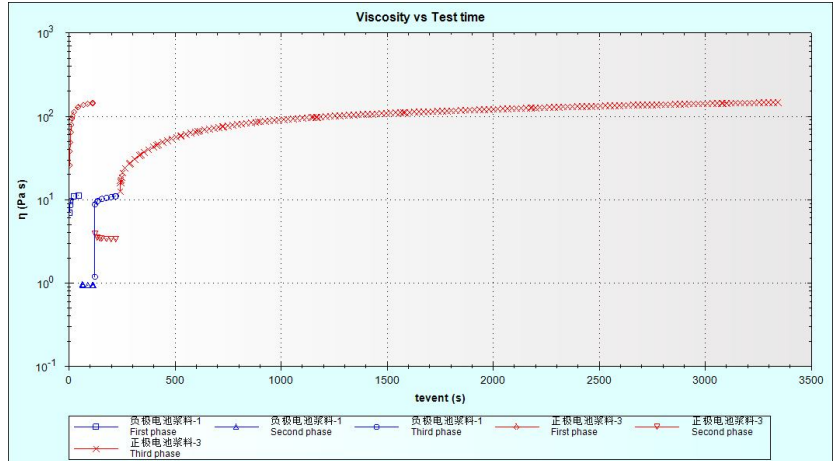
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正极与负极材料剪切粘度曲线对比

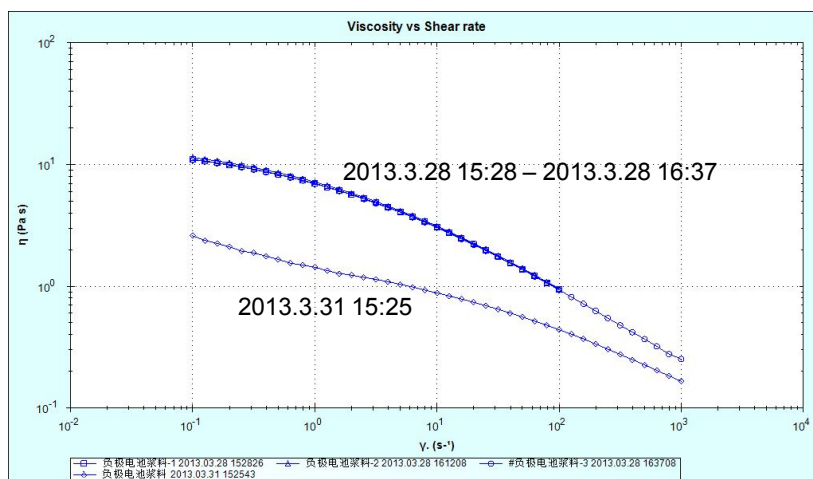


正极与负极材料触变性曲线对比



Sample Description	Action Name	Mean Value	Shear viscosity(Pa s)	Time (action)(s)
负极电池浆料-1	Rebuild time		10.10	29.0380372
正极电池浆料-3	Rebuild time		130.7	2.09486072E+003

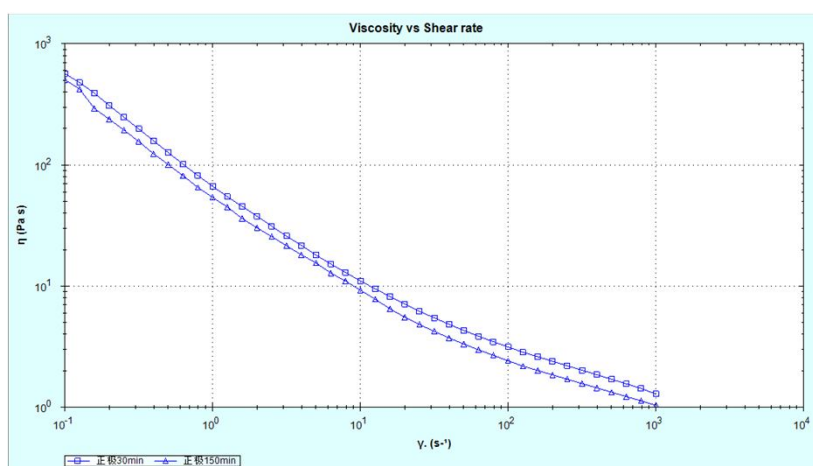
储存时间对负极浆料流变特性的影响



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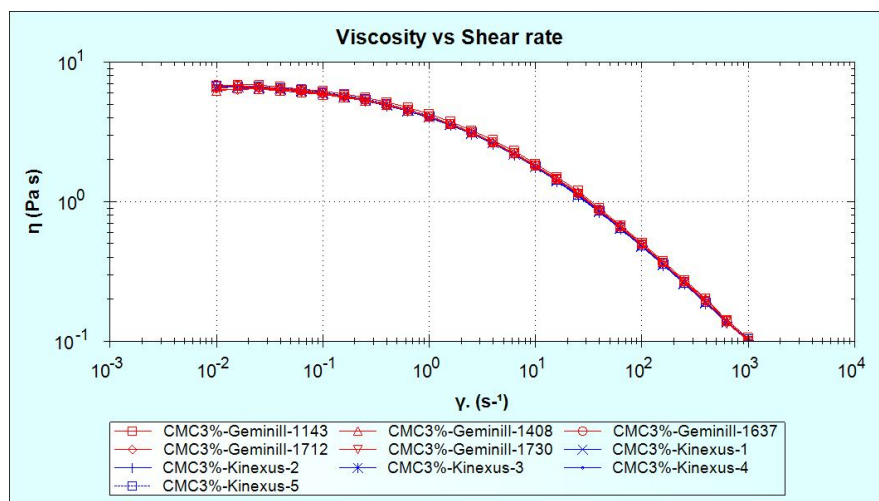
正极浆料-不同混合时间对流变特性的影响



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CMC 溶液



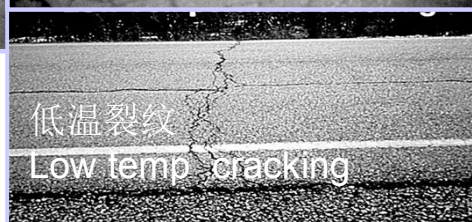
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公路行业-沥青 (Asphalt performance)



低温间:

- 模量太低
- 相位角太高

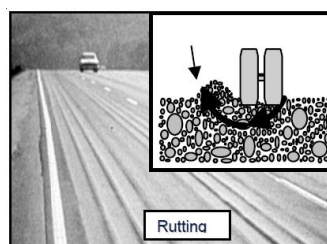


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公路行业-沥青-车辙 (M320 Binder Specification)

Performance Grade
Average 7-day Maximum Pavement Design Temperature, C
Minimum Pavement Design Temperature, C
Flash Point Temp, T48: minimum C
Viscosity, ASTM D 4402: ^b Maximum, 3 Pa-s (3000 cP), Test Temp, C
Dynamic Shear, TP5: ^c $G^*/\sin \delta$, Minimum, 1.00 kPa Test Temperature @ 10 rad/s, C
Rolling Thin Film Oven (T240)
Mass Loss, Maximum, %
Dynamic Shear, TP5: ^c $G^*/\sin \delta$, Minimum, 2.20 kPa Test Temp @ 10 rad/sec, C



Spec Requirements to Control Rutting

Tank Original Binder:

$$G^*/\sin \delta \geq 1.00 \text{ kPa}$$

RTFOT Aged Binder:

$$G^*/\sin \delta \geq 2.20 \text{ kPa}$$



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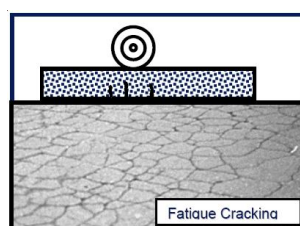
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沥青-疲劳开裂 (M320 Binder Specification)

PAV Aging Temp, C
Dynamic Shear, TP5:
$G^* \sin \delta$, Maximum, 5000 kPa
Test Temp @ 10 rad/sec, C
Physical Hardening ^e
Creep Stiffness, TP1: ^f
S, Maximum, 300 MPa
m-value, Minimum, 0.300
Test Temp, @60 sec, C
Direct Tension, TP3: ^f
Failure Strain, Minimum, 1.0%
Test Temp @ 1.0 mm/min, C

$$G^* \sin \delta \leq 5000 \text{ kPa}$$

Specification requirement
to control fatigue cracking



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食品领域



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流变学在食品领域的应用

- › 食品加工工艺设计和设备设计，比如挤出，管道输送、混合等.....
- › 产品开发过程中确定不同组分的功能
- › 中间产品或最终产品的质量控制
- › 根据消费者的爱好，进行感官评价，如人造奶油的铺展性、牛乳的粘度.....
- › 储存稳定性，货架期
- › 本构方程的建立



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冰淇淋– Scoopability 易舀性

- 测试温度：-10° C

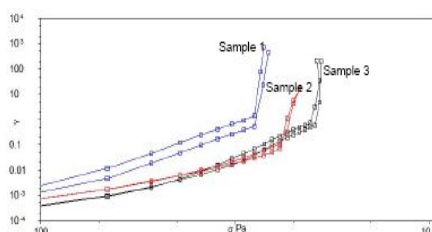


Figure 2: Plots of shear stress vs strain for the three ice cream samples. The yield stress occurs at the large gradient change from the initial slope.



Sample number	Yield stress (Pa)	Panel perception 'Ease of scooping 1-10'
1 - blue	1258	6
2 - red	1851	5
3 - black	2587	3

Table 1: Yield stress and taste panel results.

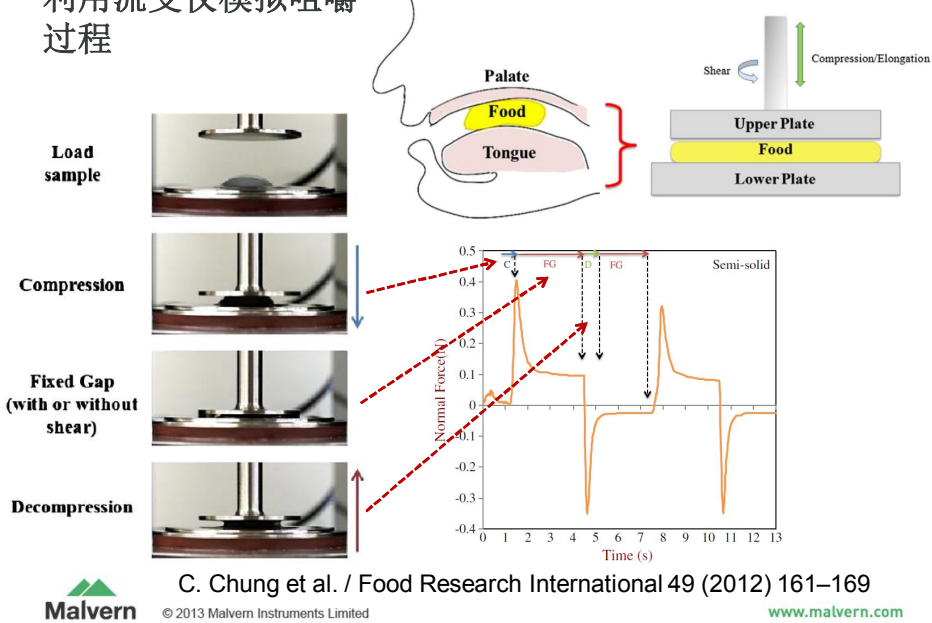
Note: 10 is easiest to scoop



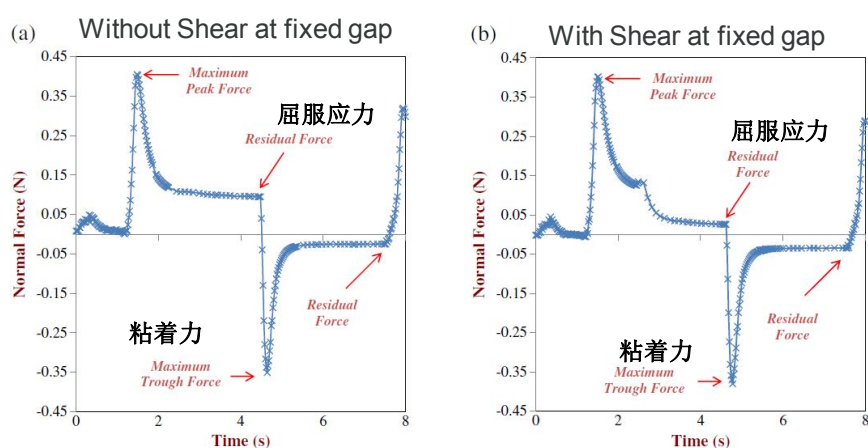
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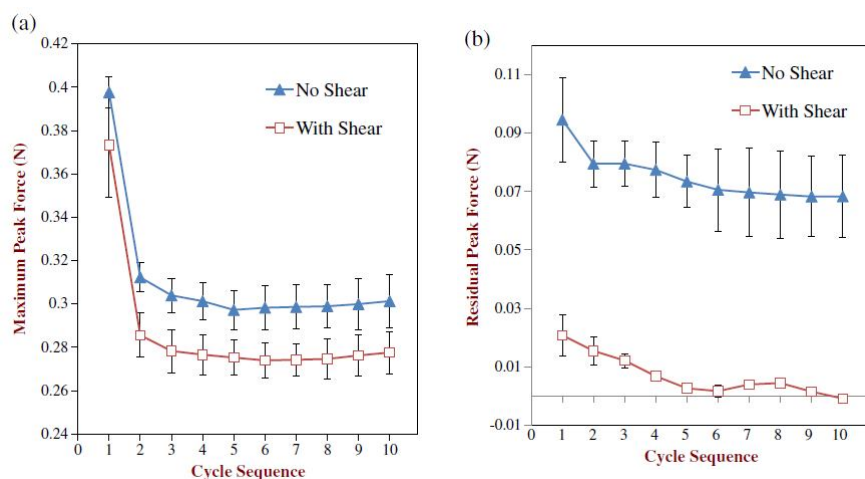
利用流变仪模拟咀嚼过程



利用流变仪模拟咀嚼过程-半固体食品



利用流变仪模拟咀嚼过程-半固体食品



› 5 wt.% gelatinized starch suspensions

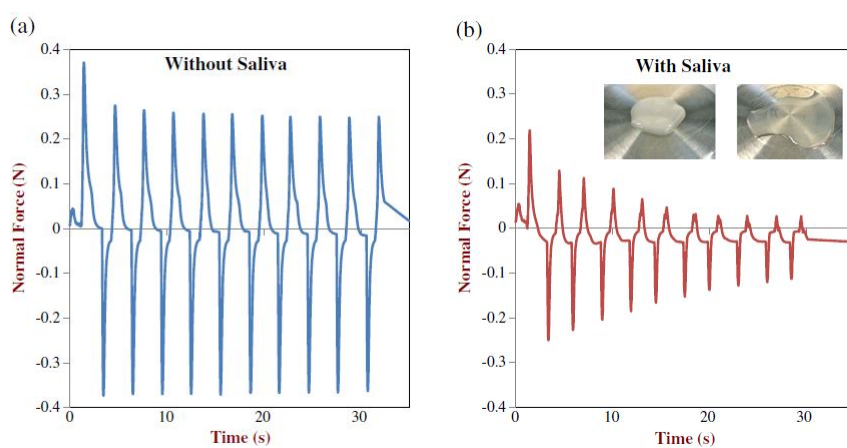


C. Chung et al. / Food Research International 49 (2012) 161–169

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利用流变仪模拟咀嚼过程



› 5 wt.% gelatinized starch suspensions

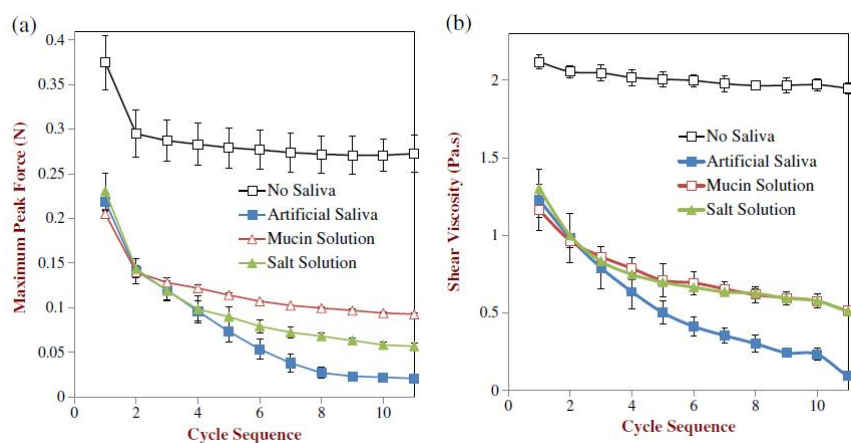


C. Chung et al. / Food Research International 49 (2012) 161–169

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利用流变仪模拟咀嚼过程



› 5 wt.% gelatinized starch suspensions



C. Chung et al. / Food Research International 49 (2012) 161–169

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生物医药领域



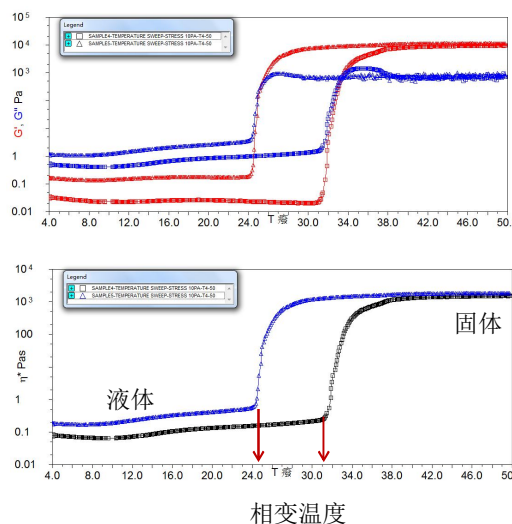
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药物制剂辅料 - 泊洛沙姆 (Poloxamer) 溶液

泊洛沙姆(Poloxamer)

- 聚氧乙烯聚氧丙烯醚嵌段共聚物，商品名为普流尼克 (Pluronic)，是一类新型的高分子非离子表面活性剂
- 作为一类优良的药物制剂新辅料，泊洛沙姆具有优良的物化特性和无毒害特点，作为乳化剂和稳定剂、增溶剂、吸收促进剂和缓释材料，广泛用于制药工业。



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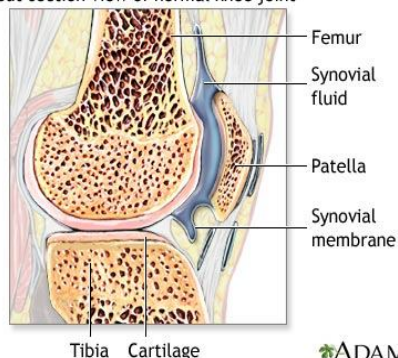
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医药行业-骨关节液 (透明质酸)

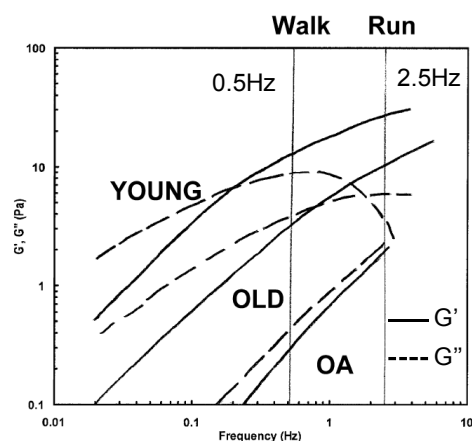
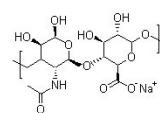
骨关节液中主要的成分是透明质酸钠

- 润滑，缓冲

Cut-section view of normal knee joint



ADAM



H. Fam et al. / Rheological properties of synovial fluids, Biorheology 44 (2007) 59–74



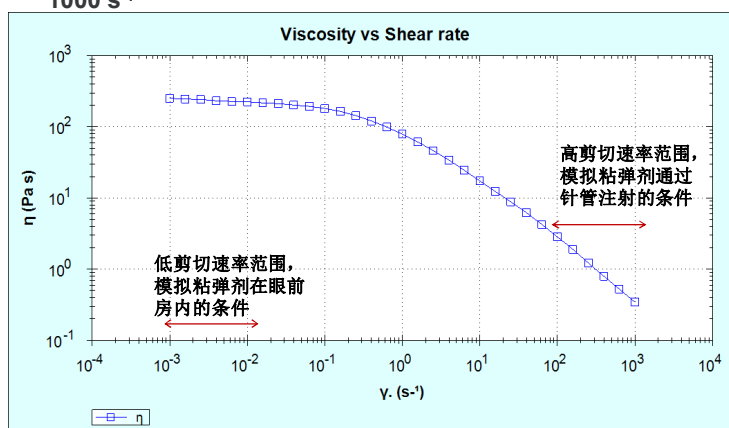
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透明质酸

眼科用透明质酸

- 温度25℃，锥板直径20mm，锥角2度，剪切速率范围 $0.001 \text{ s}^{-1} \sim 1000 \text{ s}^{-1}$



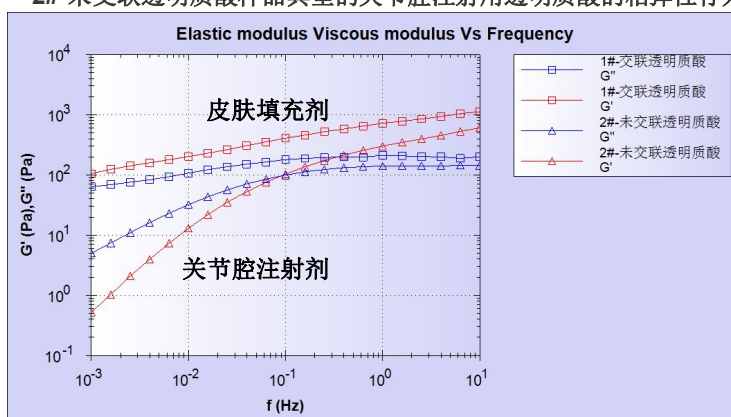
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透明质酸

两种透明质酸样品

- 1#-交联透明质酸样品，典型的透明质酸类皮肤填充剂的粘弹性行为
- 2#-未交联透明质酸样品典型的关节腔注射用透明质酸的粘弹性行为



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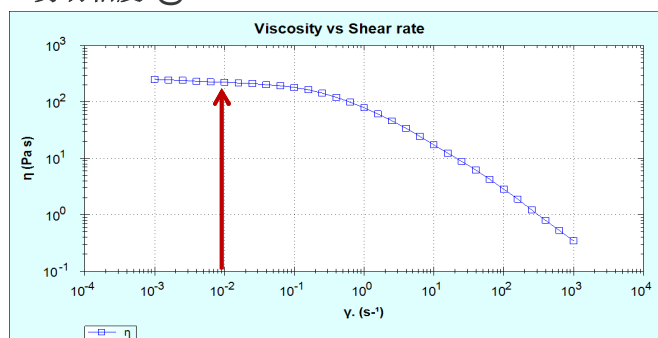
透明质酸

› 眼科用粘弹剂

- 剪切粘度 @ $0.01 \text{ s}^{-1} \geq 200\,000 \text{ mPa}\cdot\text{s}$

› 骨科用注射剂

- 剪切粘度 @ $0.01 \text{ s}^{-1} \geq 20\,000 \text{ mPa}\cdot\text{s}$



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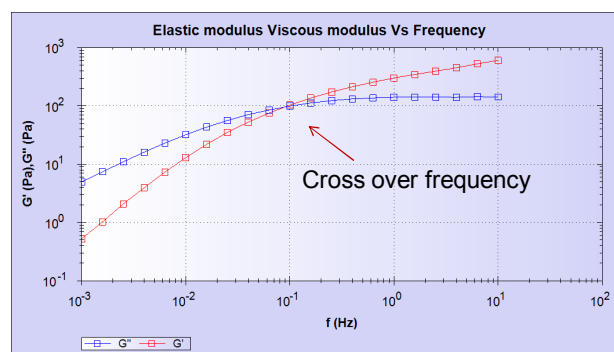
透明质酸

› 眼科用粘弹剂

- G' 和 G'' 交点频率 $\leq 0.5 \text{ Hz}$

› 骨科用注射剂

- G' 和 G'' 交点频率 $\leq 1.0 \text{ Hz}$

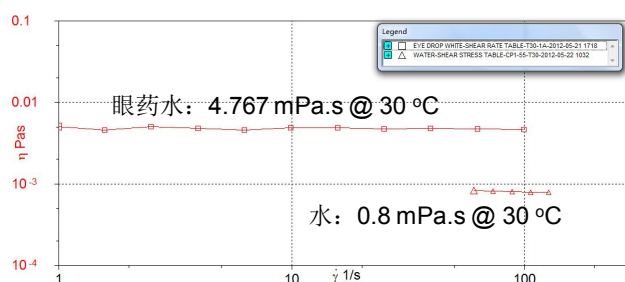
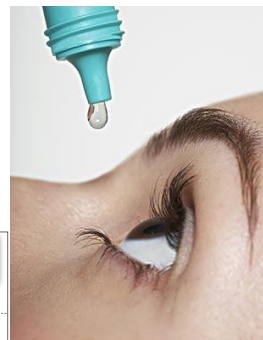


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医药行业-眼药水

- 传统眼药水由于眼睑眨动和泪液分泌，溶液型滴眼液滴入眼中会立即稀释或流失，只有1%-10%的生物利用度。

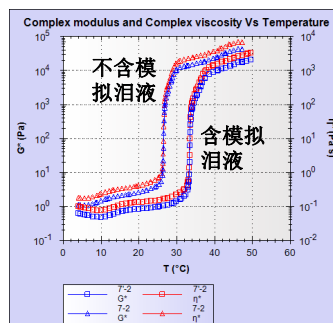
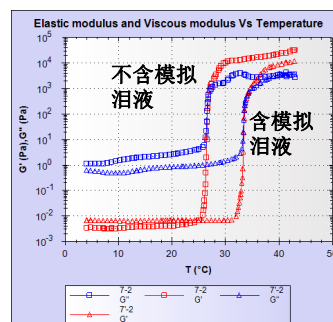


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新型眼药水 - 眼用凝胶

- 新型眼用凝胶能够提高生物利用率
 - 眼用即形凝胶在体外为液体形式，滴入眼内因温度升高短时间内由溶液变为在眼睛里形成原位凝胶黏度较大的凝胶或类凝胶状态，附着于眼睑，滞留眼部时间延长，增加了药物的吸收和生物利用度减少了使用次数



- 7: 不含模拟泪液
- 7': 含模拟泪液

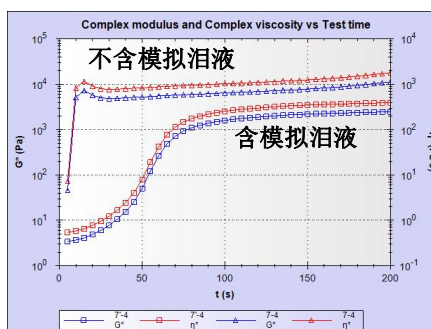
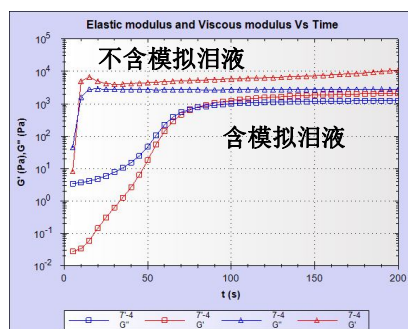


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新型眼药水 - 眼用凝胶- 凝胶时间和凝胶强度

- › 温度: 34 °C
- › 7: 不含模拟泪液
- › 7': 含模拟泪液

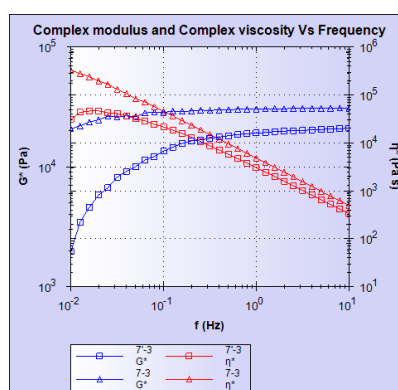
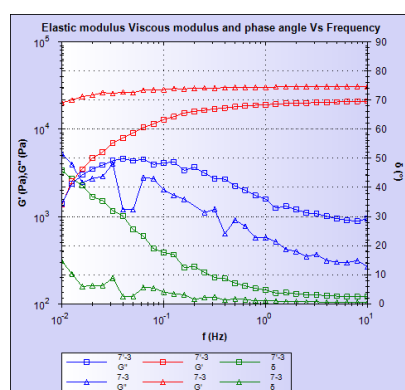


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新型眼药水 - 眼用凝胶- 剪切变稀

- › 温度: 34 °C
- › 7: 不含模拟泪液
- › 7': 含模拟泪液



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流变学研究材料分类

› 分散体系

- Zeta 电位
- 粒度分布 (PSD)
- 颗粒形态
- 平均粒径
- 浓度
- 聚合物改性剂
 - 见聚合物

› 高分子材料

- 平均分子量
- 分子量分布 (MWD)
- 支化程度
- 浓度
- 填料
 - 见分散体系

流变学表征材料的微观结构与宏观性质之间的关系



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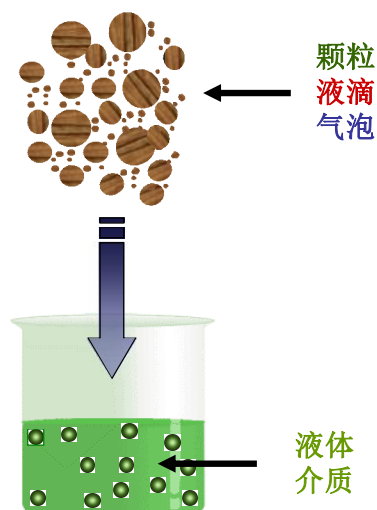
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分散体系 (Dispersions)

悬浮体系 – 固体颗粒悬浮在液体介质中

乳液体系 – 液滴悬浮在另一种液体介质中

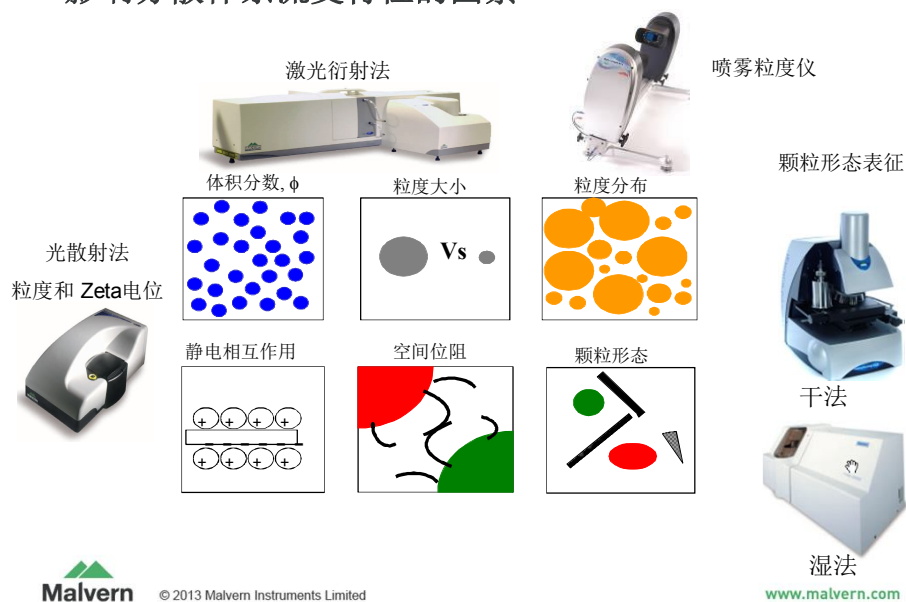
泡沫 – 气体悬浮在液体介质中



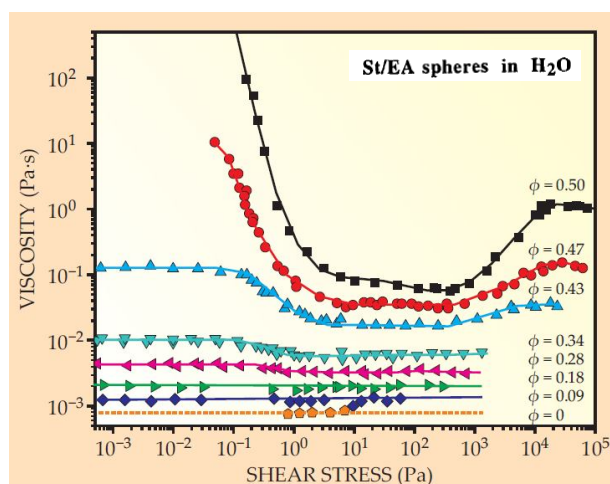
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影响分散体系流变特性的因素

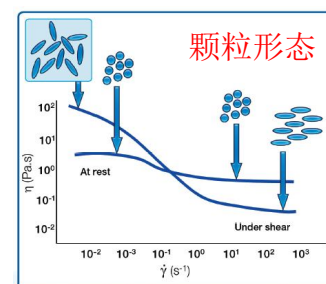
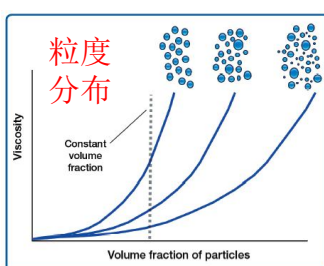
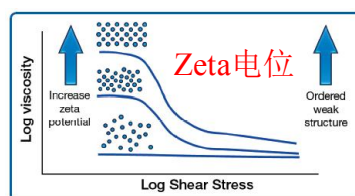
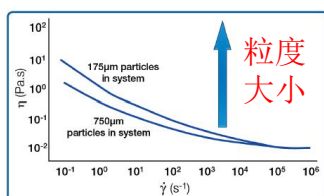


分散体系内部结构与流变特性的关系



M. Laun, *Angew. Makromol. Chem.* **123**, 335 (1984).

分散体系内部结构与流变特性的关系



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欢迎大家提问！
谢谢！

杨凯

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流变产品专家

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