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剪切诱导羟丙基纤维素取向制备各向异性水凝胶

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纤维素、海藻酸钠等天然高分子溶液在一定的浓度以上呈现液晶态，但是不具备长程有序^[1, 2]。通过一定方法形成大尺度各向异性结构可以使材料具有特殊的光学、力学性能。但是羟丙基纤维素（HPC）浓溶液黏度高，难以通过外加电场、磁场等方式形成取向结构。我们利用剪切诱导半分子链取向从而实现结构长程有序化，链段松弛之前通过凝胶化固定其结构得到各向异性的水凝胶^[3]。HPC 水溶液临界液晶浓度 (C_{LC}^*) 为 40wt%，分子链呈半刚性，在剪切下发生取向；剪切停止后溶液高黏度使其分子链松弛较慢，取向结构能在一定时间内保持。通过前驱溶液的光聚合及凝胶反应固定 HPC 的取向结构，得到大尺度各向异性水凝胶。通过偏光显微镜、小角 X 光散射、力学测试研究了溶胀前后水凝胶的结构特征以及光学、力学各向异性。

关键词：纤维素；水凝胶；各向异性；剪切取向；溶致液晶

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Anisotropic hydrogels prepared by shear induced orientation of HPC and subsequent gelation

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Some biomacromolecules such cellulose and alginate are lyotropic liquid crystals, however, their molecular assemblies have no long-range orientation. Developing macroscopic molecular orientation can effectively render the materials with functionalities. However, the hydroxypropylcellulose aqueous solutions in liquid crystal state have very high viscosity, which cannot be aligned by using electric or magnetic field. Here, we use mechanical shear to align HPC molecules, forming macroscopic anisotropic structure, which can be immediately frozen by photopolymerization and gelation of a precursor solution. Thus obtained hydrogels show anisotropy in swelling ratio, optical and mechanical properties, which are characterized by polarizing optical microscope, small angle X-ray scattering, tensile test, etc.

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结冷胶酸化凝胶粘弹特性研究

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肥胖已成为全球性威胁健康的重要原因之一, 利用亲水性胶体制成不影响口感的液态或半固态食品, 并使其在胃部的酸性环境下快速形成凝胶就可以有效延长消化时间, 有望成为控制肥胖患者的热量摄入的有效途径。传统的胶凝剂如琼脂、卡拉胶在低pH值时凝胶能力会消失, 本文以结冷胶为研究对象, 采用葡萄糖酸内酯(GDL)为酸化剂, 制备了酸化凝胶, 考察了基体浓度、GDL浓度对结冷胶酸化凝胶粘弹行为、保水性的影响。研究结果表明, GDL酸化为缓慢酸化过程, 其酸化过程符合一级动力学方程。基体浓度越高, GDL浓度越大, 酸化凝胶的凝胶时间越短。基体浓度增大, 酸化凝胶的断裂应力、杨氏模量和保水性升高, 断裂应变减小。断裂应力、杨氏模量和保水性随着GDL浓度的增大出现先增大后降低的变化趋势。GDL浓度越低, 酸化凝胶的变形性越好。酸液浸泡对酸化凝胶结构影响显著。

关键词: 结冷胶; 酸化凝胶; 断裂应力; 杨氏模量

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Study on viscoelastic properties of acid-induced gellan gels

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The influence of polymer concentrations, GDL concentration on the viscoelastic properties of low acyl gellan gels formed by acidification with glucono- δ -lactone (GDL) were investigated. The acidification of GDL can be simulated by the first order kinetic equation. Raising the polymer and GDL concentration decreased the time taken to reach gel point. Fracture stress, initial Young's modulus and water holding capacity increased while fracture strain decreased as the gellan gum concentration increased. Meanwhile, fracture stress, initial Young's modulus and water holding capacity increased with increasing GDL until GDL reached a critical level, after which further increases in GDL resulted in a reduction of fracture stress, initial Young's modulus and water holding capacity. The lower GDL concentration, the better deformability. Post-production exposure to an acidic environment was found to affect gel structure significantly.

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剪切场下纳米复合弹性体共混体系的结构演变与机理

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利用流变学和显微学方法研究了纳米填料对溶聚丁苯橡胶/低异丙烯基含量聚异戊二烯(SSBR/LPI)弹性体共混体系相行为的影响,探讨了剪切场下及剪切停止后,填料的含量和几何结构对三元共混体系相分离温度、相分离动力学以及相形貌演化的影响。研究结果表明,OMMT可以有效地减慢共混体系的相分离动力学过程,降低表观相分离温度,减小分散相的尺寸。润湿参数分析可知OMMT片层可分散在两相界面处并且起到增容剂和物理阻隔作用,有效地抑制了相区的粗化和聚并,稳定共混体系的相形貌。利用Palierne模型和Gramespacher-Meissner(G-M)模型分析证明了OMMT可以降低界面张力,并抑制了液滴相的松弛行为,通过“海-网-鱼”模型阐明OMMT的物理阻隔效应对相分离过程中相形貌演化的影响。剪切场下及剪切停止后气相二氧化硅(SiO_2)对SSBR80(80/20 SSBR/LPI)体系相形貌演化和流变行为的影响受剪切场强度的影响。弱剪切作用下, SiO_2 纳米粒子可以起到界面改性剂和物理阻隔作用,有效地抑制了相区的聚并,导致体系内形成尺寸和变形程度都很小的液滴相。强剪切作用下, SiO_2 纳米粒子起到界面改性剂的作用,不会影响到体系内细丝相的形成。剪切停止后, SiO_2 不会改变共混体系的相分离机理,但会减慢取向液滴相的松弛行为,稳定共混体系的相形貌。通过分析OMMT和气相 SiO_2 的几何形态,讨论了几何形态与剪切场协同作用对三元共混体系的结构演变的影响。

关键词: 共混体系; 纳米填料; 剪切场; 形态演化; 几何形态

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Structure Evolution and the mechanism of Styrene-butadiene rubber/Polyisoprene/Filler Ternary blends under Shear

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The influence of nanoparticle geometry, such as size and shape, on the phase morphology of partially miscible binary polymer blends under and after shear has been examined by rheological and rheo-optical techniques. The phase morphologies of the solution-polymerized styrene-butadiene rubber and low vinyl content polyisoprene (SSBR/LPI) blend systems were affected by the dispersion status of fillers which were determined by filler shapes and shear strength.

Keyword: filler geometry; SSBR/LPI/filler composites; phase morphology evolution

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SWNTs/PANI 复合纳滤膜的制备及气体分离研究

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碳纳米管 (CNTs) 具有优异的机械强度、化学稳定性以及原子级光滑内表面结构, 可大大降低气体通过时的吸附力和摩擦力, 因此以单壁碳纳米管 (SWNTs) 为作为过滤通道并填充聚合物的复合纳滤膜, 有望获得较高的输运速率和良好的气体选择性分离效果。本文采用抽滤/电场协同法制备 SWNTs/PANI 复合膜, SWNTs 除了在抽滤形成的剪切力作用下有序排列, 还因介电泳效应使其沿着电场的方向定向排列。为了提高 SWNTs 在复合膜中的分散均匀性及垂直有序程度, 采用浓硝酸/浓硫酸的混和酸液对 SWNTs 进行不同程度的功能化(接枝羧基和羟基的), 获得了不同极性的 SWNTs。结果表明, 极性程度越高的 SWNTs 在电场作用下越容易取向, 制备的 SWNTs/PANI 复合膜中其垂直有序程度越高, 气体分离效果及选择性也越好。

关键词: 纳滤膜; 碳纳米管; 功能化

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Study on Fabrication and Gas Separation of SWNTs/PANI Composite Membranes

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Carbon nanotubes (CNTs) possess excellent mechanical strength, chemical stability and atomically smooth interiors. As filtrating channels, the adsorption and friction can be greatly minimized when the gases pass through so that SWNTs/polymer composite membranes have good prospects for gas transport and selective separation. In this work, SWNTs/PANI composite membranes were prepared by a filtration-electric synergy method. The SWNTs tends to align vertically by shear force formed by filtration as well as dielectric electrophoresis effect under the electric field. To improve the dispersion and verticality of SWNTs in composite membranes, chemical functionalization of SWNTs was recognized by a mixing acid with concentrated nitric acid and sulfuric acid. The distinct functionality of SWNTs (grafted with carboxyl and hydroxyl groups) were obtained with different polarity. With increasing polarity of SWNTs, the electrical field induced translational motion of polar SWNTs along the field direction and the SWNTs/PANI composite membrane exhibited a better performance on gas separation and selectivity.

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支持向量机预测聚合物粘度方法研究

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摘要: 聚合物驱油主要机理之一是扩大波及系数, 聚合物通过增加水相粘度, 降低水油流度比, 克服驱替相的“指进”现象, 从而改善油层横向及微观孔隙结构的非均质状况, 提高垂向波及效率, 以油田使用聚合物为例, 系统研究各因素对聚合物流变性影响, 对数据进行分析, 建立数学模型, 在聚合物溶液流变性实验的基础上, 分析聚合物溶液表观粘度变化规律, 应用支持向量方法预测聚合物粘度, 为聚合物驱油供理论基础。

关键词: 聚合物 粘度 支持向量机 模型

聚合物流变性质受聚合物的分子质量、溶液的含盐量、质量浓度、温度等因素的影响。60年代以来国外对聚合物溶液的流变性质进行系统和深入的研究, 建立起若干流变模式。其中大部分研究限定在聚合物的粘滞特征上, 由于聚合物分子结构和构象极为复杂, 许多学者在实验研究的基础上建立经验流变模型, 如幂律、Meter、Cross、Ellis模型等。国内王立军、唐金星、王新海、李彩虹等人系统的研究了聚合物的相对分子质量、浓度、矿化度等因素对聚合物溶液流变性的影响, 建立了描述聚合物溶液粘弹性的半经验模型, 给出了实验条件下聚合物溶液的流变参数随其相对分子质量、浓度及温度变化的模型。针对现场应用复杂情况, 通过室内实验研究, 应用支持向量机方法预测聚合物粘度为现场应用提供技术指导。本研究功法发现:

(1) 相同浓度、剪切速率和矿化度下, 聚合物溶液的表观粘度随着温度的增加均下降, 当温度高于临界温度点时, 即呈现为牛顿流体的流动状态, 粘度不再随剪切速率变化而变化;

(2) 相同矿化度、温度和剪切速率下, 聚合物溶液的表观粘度随其浓度的增加而呈增加的趋势, 聚合物溶液具有明显的增稠特性, 其质量浓度越高, 增稠效果越明显, 聚合物溶液的表观粘度随浓度增加而增大的速率是不同的。当聚合物溶液的浓度较低时, 表观粘度随浓度增加而增大的速率较小, 当浓度较高时, 该速率变大;

(3) 相同浓度、温度和矿化度下, 聚合物溶液的表观粘度随着剪切速率的增加而下降。聚合物溶液在所测定的剪切速率范围内, 都表现出表观粘度随剪切速率增大而降低的明显假塑性流变行为特征;

(4) 聚合物的粘度受浓度、温度、矿化度、剪切速率等因素的影响, 是多种因素的综合作用, 在不同的条件下, 存在一个影响聚合物溶液粘度的敏感因素;

(5) 支持向量机方法综合各因素, 可以较好的预测聚合物流变性。

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挤出流场中高分子应力松弛行为的双时间尺度关联[☆]

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在压力稳定型迭代分步算法框架下, 采用DEVSS/SU方法计算了高分子熔体在挤出流道中的复杂流变行为。计算得到了外力作用下流场中高分子的主链拉伸分布(见图1), 并提出了揭示挤出自由面上高分子应力松弛的数学模型, 将熔体的宏观流动时间 t 与细观分子的本征弛豫时间 λ_s 两个时间尺度进行了恰当的关联(见图2), 这对深刻理解和定量描述高分子的拉伸流动和松弛行为具有重要意义。

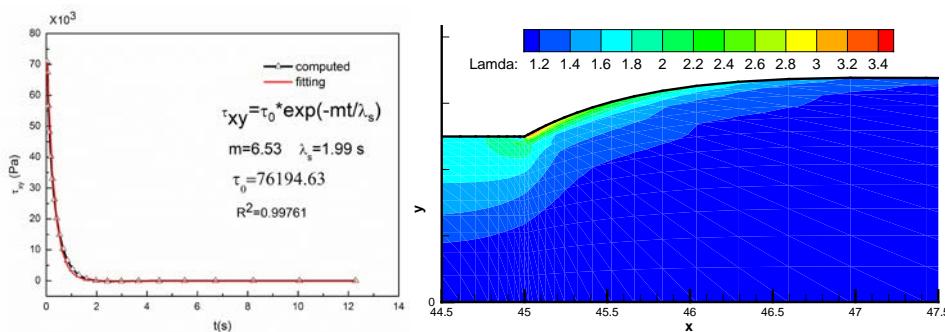


Fig. 1 Calculated backbone stretch distribution of the extrusion flow for S-MDCPP model.

Fig. 2 Evolution of stress relaxation with time along the extrusion free surface.

关键词: 高分子熔体; 流变行为; 挤出流动; 数值模拟

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Two timescale linking the stress relaxation behaviors of polymer melts in the extrusion flow

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The complex rheological behavior of polymer melts in the extrusion flow is calculated by using the DEVSS/SU method within the frame of pressure stabilized iterative fractional algorithm. The stretch distributions of backbone induced by the external force are predicted. It is significant that a method to link the macroscopic extrusion flow time with the stretch relaxation time of mesoscopic macromolecules is proposed, so as to deeply understand and quantitatively describe the extensional flow and rheological behaviors of branched polymer melts.

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分步控制的流动场诱导聚乳酸共混物原位纳纤化

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高分子共混物两相间热动力学不相容性往往导致相形态难以控制和界面结合较差, 进而力学强度和延展性难以平衡。我们以全降解型聚乳酸/聚丁二酸丁二醇酯(PLA/PBS)共混物为研究模型, 采用分步耦合机制, 首先, 利用挤出共混中的拉伸/剪切流动场, 依次实现了分散相的共连续化和预取向。通过流变测试结果显示, 当PBS含量从10%增至60%时, 在低频区损耗因子具有频率依赖性, 表明形成了网络结构, 这与扫描电镜观察结果一致。进一步, 利用注塑成型中的高压剪切流动场, 我们实现纳米分散相的纳纤化, 其尺寸约为100nm。同时获得了力学强度和延展性的显著提高。随着PBS含量从10%, 20%, 40%增加到60%, 相对于纯PLA的冲击强度(5.6 MJ/m³), PLA/PBS纳纤复合材料分别提高1256%、3039%、1822%和7133%; 而断裂伸长率分别是纯PLA(5%)的13.4、31.6、23和75倍。另外, 尽管PBS的拉伸强度只有35MPa, PLA/PBS复合材料的力学强度依然能够达到69MPa。由此可见, 我们设计的分布控制的流动场能够作为聚乳酸高性能化和多功能化的基础策略。

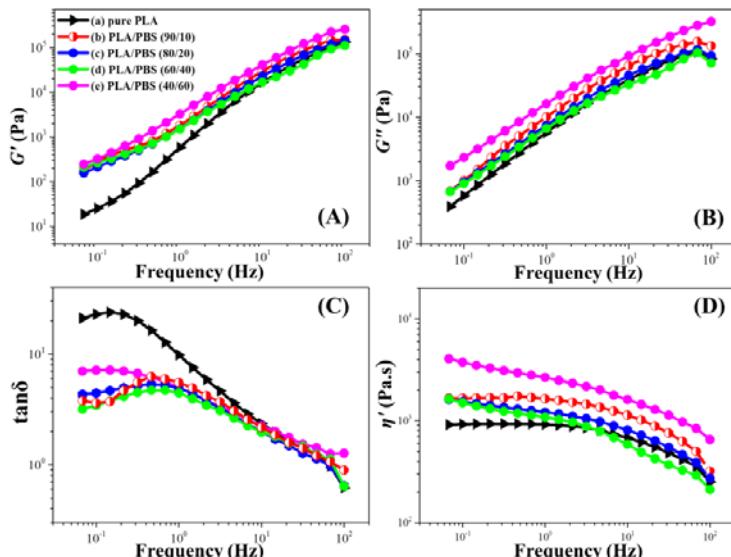


Figure 1. Viscoelastic behaviors determined at 180 °C for PLA/PBS blends. Frequency dependency of (A) dynamic storage modulus (G'), (B) dynamic loss modulus (G''), (C) loss tangent ($\tan \delta$) and (D) complex viscosity (η) for (a) pure PLA, (b) PLA/PBS (90/10), (c) PLA/PBS (80/20), (d) PLA/PBS (60/40), PLA/PBS (5/50) and PLA/PBS (40/60) blend samples.

关键词: 流动场; 聚乳酸; 聚丁二酸丁二醇酯; 纳米纤维;

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激光全息聚合物分散液晶的光固化流变行为

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全息聚合物分散液晶 (HPDLCs) 在3D显示、信息存储、安全防伪、传感器和调制激光等高新技术领域应用广泛, 其结构的形成受到全息记录过程中液晶扩散、液晶成核与复合体系凝胶化过程的影响, 因此优化复合体系的光固化流变行为非常关键。本文系统研究了传统Irgacure 784/BPO光引发体系¹和新型光引发阻聚剂 (photoinitiator)²⁻⁴对HPDLCs光聚合动力学与光固化流变行为的影响。利用光引发阻聚剂对光固化流变行为的调控作用, 显著提高了HPDLCs的相分离程度, 实现了裸眼可见的3D全彩色图像存储。在此基础上, 研究了超支化单体、ZnS纳米粒子、POSS等因素对HPDLCs光固化流变行为的影响。

关键词: 全息聚合物分散液晶; 光引发阻聚剂; 光固化流变行为

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Photorheology of holographic polymer dispersed liquid crystals

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Holographic polymer dispersed liquid crystals (HPDLCs) are of immense utility in a myriad of high-tech areas, such as 3D display, data storage, anti-counterfeiting, sensors and mirrorless tunable lasers. Since the HPDLC formation is highly dependent on the LCs diffusion, LCs nucleation, and photopolymerization gelation during holographic recording, it is extremely critical to optimize its photorheology. Herein, the effects of traditional Irgacure 784/BPO photoinitiating system and novel photoinitiator on the photopolymerization kinetics and photorheology were systematically investigated and compared. Results show that the photoinitiator exhibits good control capability over the photorheology, thus leads to greatly improved phase separation in HPDLCs, as well as the successful reconstitution of visually identifiable colored 3D images to the naked-eye. Furthermore, the influences of hyperbranched monomer, ZnS nanoparticles, POSS and other components on the photorheology in HPDLCs were also studied.

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相容性聚合物共混物的分子图像

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在聚合物相容性共混物中，例如A/B二元混合物，由于共混组份本身固有的动力学特性（例如，纯熔体中A链段和B链段具有不同的摩擦系数及其温度依赖性），以及A链段的局部摩擦环境会受到B链段的影响，因此给定组份表现出摩擦系数以及它的温度依赖性不同于本体并且随浓度变化，B的情况亦然。Lodge和McLeish (LM模型) 提出的自浓度模型强调大分子主链连接性，认为在控制给定链段摩擦系数的局部体积中，任意组份的局部浓度总是大于其宏观平均浓度。有效局部浓度与宏观平均浓度的差别通过材料参数-自浓度联系起来。该模型可定性解释聚合物相容性共混物动力学的非均质性。因此，如何定量地确定组份的有效局部浓度是相容性共混动力学研究的核心问题。对于共混物的有效局部浓度，当考虑聚合物交叠浓度对分子量内贡献和分子间贡献的影响，我们修正了LM模型中关于有效局部浓度、平均浓度和自浓度的相互关系。针对聚合物溶液、共混物在Kuhn尺度的局部堆砌方式，考虑分子内和分子间贡献，可以解释相容性共混物中自浓度的分子结构依赖性。也发现共混物中浓度涨落的温度依赖性由Flory参数控制。

关键词：聚合物；相容性共混；动力学

Molecular Picture of Effective Local Concentration in Miscible Polymer Blends

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For polymer solutions and miscible blends, we introduced the correlation length and the overlap concentration as the boundary conditions to estimate the effective local concentration. Moreover, the polymer species-dependence and the blend partner-dependence of the self-concentration in miscible blends can be understood from details of the local packing (molecular properties related to chain dimensions) inside the Kuhn length lK^3 . The temperature-dependence of the effective concentration and concentration fluctuations are controlled by the Flory-Huggins interaction parameter. A complete molecular picture of the effective local concentration is presented herein.

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纳米纤维素晶体形态的流变学表征

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纤维素纳米晶体(Cellulose Nano-Crystal, CNC)是从纤维素中提取的一种直径在5-20nm, 长度在100nm到几个微米的棒状晶体, 在纳米增强材料与功能材料领域有重要应用价值^[1]。长径比为CNC最重要的性能指标, 目前主要通过电镜显微观察统计法表征, 该方法直观可见, 但存在着测量工作量大、周期长、统计数据有随机性等不足。本研究采用乌氏粘度计考察了不同CNC表面电荷密度与外加盐(NaCl)含量对CNC悬浮液特性粘数的影响, 并通过Simha模型^[2,3]拟合了CNC的长径比; 研究结果表明, 随着NaCl浓度增加(或者CNC表面电荷密度下降), CNC悬浮液稳定性下降, 特性粘数出现了先降低后上升的变化, 这主要是少量NaCl屏蔽CNC表面的离子双电层, 而过量NaCl促使CNC聚集所致。在一定CNC表面电荷密度与NaCl含量下, 通过流变法所得的CNC长径比与透射电镜(TEM)统计结果非常接近, 表明流变法是一种表征CNC长径比的可行方法, 且在测试时间、表征条件和统计权重上有明显优势。

关键词: 纳米纤维素晶体; 长径比; 流变学; 特性粘数

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Characterization of cellulose nanocrystal morphology by rheology method

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Abstract: The objective of this study is to use rheology as a simple method for cellulose nano-crystal (CNC) morphology characterization. In order to give accurate CNC morphology, the influence of NaCl concentrations on the stability, effective diameter and rheological behavior were investigated by dynamic light scattering and Ubbelohde viscometer. With NaCl concentration increasing, the stability of CNC suspensions decreased, while the effective diameter and intrinsic viscosity first decreased and then increased. This phenomenon was attributed to screening effect of double electric layers on CNC at lower NaCl content, and promoting CNC aggregation at higher NaCl content. CNC aspect ratio calculated by Simha model was very close to that of TEM statistical results, which indicated that the rheological method is a viable method for CNC aspect ratio characterization.

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聚合物在线流变测量解决方案

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在线粘度测量是目前很多化妆品、食品、石油、化工、电子、造纸等行业中应用越来越广泛的技术，在线粘度的测量方法很多，主要有毛细管式、旋转式、振动式、注塞式等，而测量对象、流体的流变特性、应用面也各不相同。从仪器和流变学的角度出发，对在线粘度测量的方法、流体的流变学类型进行了分析，并提出了相应在线流变测量解决方案。

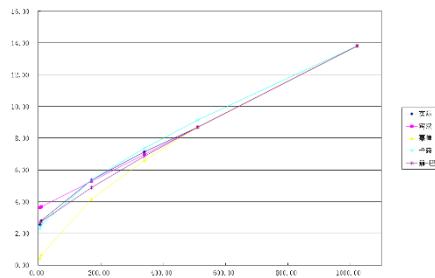


Fig. 1 Shear Rate – Shear Stress Rheology Model

关键词：在线粘度；流变学；牛顿流体；非牛顿流体；在线流变

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Process rheology solution for polymer

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Online viscosity measurements are used in petroleum, chemical, food, electronic and paper. Online viscosity measurement method is different. There is capillary, rotary, vibration, bib type, etc., and the measurement of the object also each are not identical, fluid rheological properties also each are not identical, applications are also different. This article from the rheological view and online viscosity measurement method, fluid rheological types and discussed different online viscosity measurement methods, characteristics and application of some common industry applications concluded, and the measurement of the online viscosity of some common problems on rheological analysis, and proposes on-line rheology measurement of the processing method.

Key words: online viscosity; ; rheology; non-Newtonian liquid; process rheology

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硅烷修饰的含碳纳米颗粒电流变液

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电流变液的流变特性可随外加电场快速连续可逆地调控，从而可实现高效的电力转换。本文报告了我们最近开发了表面接枝长链硅烷的一维纳米电流变材料和表面修饰笼状硅烷的二维石墨烯基纳米电流变液，硅烷修饰有效提高了纳米颗粒在硅油中的润湿和分散，进一步降低了流体的零场粘度，提高了电流变效率和流体抗沉降性。这些高稳定的电响应纳米流体在微流体装置中有应用前景。

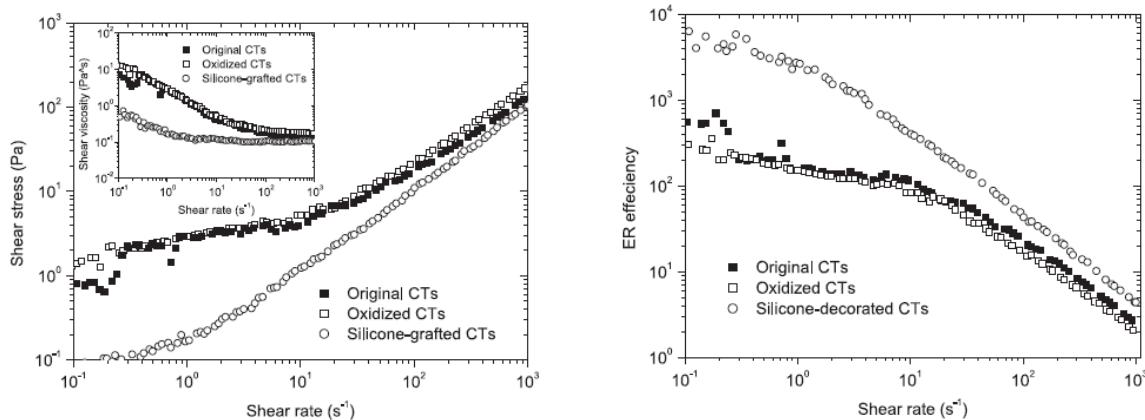


Fig. 1 Zero-field shear viscosity (left) and electric field-induced electrorheological efficiency vs. shear rate for the suspensions of original CTs, oxidized CTs, and silicone-grafted CTs ($T = 23^\circ\text{C}$, $\phi = 10 \text{ vol\%}$).

关键词：碳纳米管；石墨烯；硅烷修饰；纳米电流变液

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Nano electrorheological fluid of silicone-decorated carbonaceous nanoparticles

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We report nano electrorheological fluids based on silicone-decorated one-dimensional carbonaceous nanotubes and two-dimensional graphene oxide nanosheets, which exhibits excellent dispersion stability and enhanced electrorheological effect under electric fields. These characters make the nano electrorheological fluids possess potential use in the MEMs filed.

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粒子填充高分子复杂体系的流变学

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填充高分子体系的流变行为复杂多变，随着填料体积分数 φ 的增加，填充体系由简单的粘性流体转变为高弹性固体^[1, 2]。众所周知，在低粒子含量区，填充体系的增强效应主要归因于熔体流中固体内含物的流体力学作用^[3]。而在高粒子含量区，粒子间的直接接触控制形变，难以用简单的流体力学方程描述，而至今仍然缺乏基于真实结构的理论模型。填充体系在低频区的类液-类固转变的具体原因尚不清楚，可能的机理包括：(1) 粒子表面吸附分子链的松弛变慢；(2) 粒子间长链的桥结；(3) 低中粒子含量下粒子“拥挤网络”的形成；(4) 高粒子含量下粒子间的胶体与摩擦相互作用等。然而，我们将证明，所谓的类固和类液行为都有共同的机理，根据所提出的“两相模型”可以描述不同纳米填料填充聚合物熔体的线性动态流变行为。

关键词：粒子填充高分子复杂体系；流变学；两相模型

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Rheology of Particle-filled Polymeric Complex Systems

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Filled polymers exhibit a diverse range of rheological properties, varying from simple viscous fluids to highly elastic solids with increasing filler volume fraction φ . The effect of filling on rheology is well-known in the range of small φ where the reinforcement could be attributed to hydrodynamic effects caused by the solid inclusions in the melt stream. For high φ where direct particle contacts dominate the deformation, a straightforward solution of hydrodynamic equations is difficult and theoretical models based on the realistic structural ideas are still missing so far. The cause for the liquid-like to solid-like transition at the low-frequency zone is also still not clear. We will show, however, the so-called liquid-like and solid-like behaviors share the common mechanism, in the framework of a proposed “two phase model” applied to linear dynamic rheology of polymer melts filled with a wide range of nanosized fillers.

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含蜡原油的依时性黏弹—屈服行为研究

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黏弹—屈服特性是胶凝含蜡原油重要的依时流变特性, 对石油管输系统的流动保障具有重要影响^[1]。目前, 对凝油加载后的屈服转变行为的研究主要集中在宏观唯象描述, 缺乏力学机理上的解释, 并且其表征指标不能体现出屈服历程的复杂性。为此, 本研究基于一系列的流变学研究手段, 来探索凝油的依时性黏弹—屈服转变机理。剪切应力线性加载以及回弹测试(图1)表明, 时间尺度越长, 残余应变越大, 即损失的弹性越多, 因此测得屈服应力越小。相比于屈服应力, 屈服应变不随测量条件的变化而变化, 对表征凝油屈服更具有代表性。并且, 温度越低, 屈服应变越小, 结构越脆。为了表征加载过程中的形变随时间的积累, 基于黏弹—触变模型^[2]对能量耗散进行定量计算, 结果表明, 胶凝油结构屈服时, 存在临界能量耗散(图2), 可用以表征断裂韧性。最后, LAOS测试表明, 含蜡油具有软物质的典型力学特征, 需要多参数综合描述其复杂的黏弹—屈服转变。

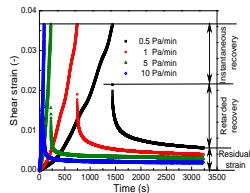


Fig. 1 Deformation and recovery at different stress ramp-up loading rate for Daqing crude oil at 32 °C.

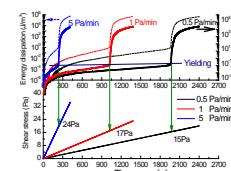


Fig. 2 Evolutions of the shear strain and energy dissipation of Daqing crude oil upon stress ramping at 32 °C.

关键词: 含蜡原油; 黏弹性; 屈服应力; 能量耗散

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Time-Dependent Viscoelastic and Yielding Behavior of Waxy Crude oils

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To understand the viscoelastic and yielding behavior of waxy crude oils has always been a critical concern in the flow assurance of petroleum pipelines. However, present studies are mainly focused on the phenomenological description, lacking the exposure of mechanical mechanism. In this study, the time-dependent yielding process was investigated by extensive rheological techniques. The experiment of stress ramp loading and its recovery showed that a lower stress loading rate leads to a higher residual strain, implying that the longer the time scale is, the more elasticity of the oil loses. The expression of critical yield strain was introduced to characterise structure failure and the fracture ductility can be evaluated by the energy dissipation derived from viscoelastic-thixotropic model. At last, it was found that the yielding transition requires a range of mechanical parameters to describe it by LAOS tests.

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接枝纳米粒子填充体系空间分布调控与弛豫行为研究

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采用细乳液聚合制备了不同接枝链长度和密度的聚苯乙烯接枝二氧化硅纳米复合粒子($\text{SiO}_2\text{-PS}$)，用以填充PS和聚甲基丙烯酸甲酯(PMMA)，考察了接枝链聚合度(N)、接枝链密度(σ)、基体链聚合度(P)以及接枝链与基体链相容性对纳米粒子空间分布的影响规律。采用宽频介电谱系统研究了复合体系链段动力学，揭示了纳米粒子周围接枝链和基体链的界面层弛豫行为。结果显示，当 $\sigma \cdot N^{0.5} \geq (N/P)^2$ 时，接枝链与基体链间相互排斥，界面层松弛远快于基体链松弛。此外，在聚合物玻璃化转变温度(T_g)附近，由于受慢的基体链松弛影响，界面层松弛时间随温度升高反而增大。

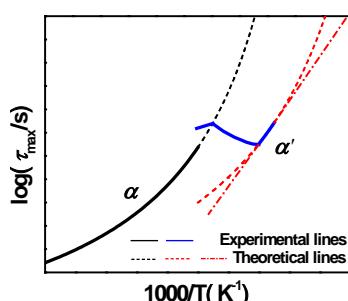


Fig. 1 Temperature dependence of α -relaxation and α' -relaxation time in polymer-grafted nanoparticle filled composites

关键词：接枝粒子；空间分布；相容性；链段弛豫

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Segmental Dynamics of Polymer-grafted Nanoparticle Composites

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Polystyrene-grafted silica nanoparticles ($\text{SiO}_2\text{-PS}$) with different grafted chain length and grafting density were prepared via miniemulsion polymerization. The spatial distribution of grafted nanoparticles (NPs) in PS and poly(methyl methacrylate) (PMMA) matrices were investigated by morphology observation. More interestingly, we probed the enhanced mobility of interfacial layer (α' -relaxation) in grafted NP filled composites. In addition, it was unexpected that the α' -relaxation time increased with increasing temperature in the vicinity of glass transition temperature (T_g) of polymer matrix. Such an anomalous temperature dependence behavior can be attributed to the influence exerted by the slower α -relaxation dynamics.

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高分子多组分体系应变诱导结晶的热力学

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高分子应变诱导结晶行为受到其它共存组分的影响。我们将Flory的溶液高分子体系熔点降低理论和拉伸高分子体系熔点升高理论结合起来, 来预测溶液拉伸高分子体系的平衡熔点随温度、浓度和溶剂品质而发生的变化。所得到的结果在我们采用动态蒙特卡罗分子模拟方法得到的起始应变行为中得到了验证。

关键词: 高分子; 应变; 结晶; 热力学

Thermodynamics of Strain-induced Polymer Crystallization in Multi-component Systems

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Strain-induced polymer crystallization is influenced by the coexisting other components. We combined Flory's thermodynamic theory on the melting point depression of solution polymers and Flory's thermodynamic theory on the melting point up-raising of stretched polymers, to predict the dependence of the melting point of stretched solution polymers on the temperature, the concentration and the solvent quality. The results were verified by the onset strains of crystallization observed in our dynamic Monte Carlo simulations of strain-induced polymer crystallization in solutions.

*国家自然科学基金面上项目的资助

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LiF 细颗粒流化特性的实验研究

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摘要: LiPF₆是制备锂电池广泛使用的电解质材料, 由 PF₅气体与固体颗粒 LiF 反应生成。本文以研究细颗粒 LiF 在流化床中的流化特性出发, 提出添加惰性粗颗粒改善 LiF 细颗粒流化质量的方法。通过在自建的流态化实验装置探讨了床层高度和分布板开孔率对流化性能的影响, 并进行了添加重晶石组分下的的 LiF 细颗粒的流态化实验研究。结果表明: 随着重晶石颗粒添加质量比例的增加, LiF 流化性能越来越好, 在粗颗粒添加量为 60%时能实现稳定流化。在相同添加量下, 添加粒径越小, 二元混合体系最小流化速度越小; 在相同粒径下, 添加量越大, 最小流化速度越小。在实验研究基础上分析了细颗粒 LiF 聚团的机理, 建立了细颗粒 LiF 聚团模型, 并对细颗粒 LiF 聚团颗粒的粒径进行了预测。还结合 R-Z 方程, 对流化质量进行了评价。

关键词: LiF; 颗粒; 流态化; 聚团

Fluidization of LiF Powers with additive Particles

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Abstract: LiPF₆ is the most widely used in lithium battery electrolyte which can be prepared by the reaction of LiF by PF₅. Experiment investigation on the fluidization characteristic of LiF powders by adding barite sands was conducted in the self-build fluidized bed equipment.. Pressure fall-off curve of increasing flow rate and decreasing flow rate achieved a good coincidence with this additive proportion. With the same addition, the particle size is the smaller, and the minimum fluidization velocity of binary mixture system is smaller; At the same particle size, the amount is larger, and the minimum fluidization velocity is smaller. Aggregating mechanism of LiF powders was analyzed on the basis of experimental research. And agglomeration sizes of LiF powders were calculated by Zhou-Li model. Calculation results revealed that fluidized agglomeration sizes of LiF powders were much smaller after adding barite sands. Verified by R - Z equation, the addition of barite particles improves the fluidization quality of LiF powers.

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基于金属配位键制备高强度物理水凝胶

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近年来, 研究者们采用不同的方法制备了多种高强度水凝胶, 大幅拓宽了这一类软材料的应用领域。通过网络结构设计以及一定的能量耗散机制, 水凝胶的韧性能够得到大幅提升^[1]。然而, 这些水凝胶中通常存在共价键交联网络, 因此加工性能较差, 难以实现回收利用。针对这一问题, 可以用具有动态可逆特征的非共价键代替化学交联制备超分子聚合物水凝胶; 常见的非共价作用有氢键、离子键、疏水缔合等^[2,3]。本文通过金属配位键交联聚合物制备高强度物理水凝胶。所制备的水凝胶拉伸断裂伸长率和断裂应力分别达到6MPa和800%。此外, 金属配位键具有响应性, 可以在一定的条件下破坏和形成, 这种动态可逆特征赋予水凝胶良好的加工性、自修复、形状记忆等功能。这种具有多功能的高强度水凝胶将在软驱动器、组织工程等领域发挥作用。

关键词: 金属配位键; 高强度; 自修复; 水凝胶

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Tough Physical Hydrogels Based on Metal-Ligand Coordination

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In the past decades, intense efforts have been devoted to fabricate hydrogels with improved mechanical properties via the design of network structure and mechanism of energy dissipation. However, it is still a challenge to develop hydrogels that achieve combination of good mechanical properties along with processability. Herein, we report meta-coordination mediated physical hydrogels with high toughness, processability, self-recovery, self-healing, and shape memory properties. The metal-ligand coordination, which can reversibly break and re-form in specific condition, is chosen as the physical cross-links. These physical hydrogels show remarkable mechanical performances; the breaking strain and stress reach 800% and 6 MPa, which are comparable to those of other tough gels. The dynamic nature of metal-coordination bonds also renders the gels with good processibility, self-healing, and shape memory properties. We believe these mechanically tough and functionally versatile gels will find applications in soft actuator, tissue engineering, etc.

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纳米二氧化硅对 PLA/PMMA 共混物链缠结和流变性的影响

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在高分子材料中引入纳米颗粒不仅能够影响材料的机械性能, 而且能显著改变材料加工过程中的流变性能。尤其对于高分子共混物, 纳米颗粒还能够引起混合物相结构的改变。我们按照不同的质量百分比将未经处理的纳米二氧化硅 (SiO_2) 颗粒通过熔融共混的方法引入到相容的PLA/PMMA 50/50的共混物中。研究发现随着二氧化硅颗粒的加入, 不仅共混物的玻璃化转变温度得到提高, 而且其玻璃化转变区间也变大。扫描电镜 (SEM) 结果显示 SiO_2 增强的 PLA/PMMA 混合物的界面存在明显的“坑状”结构。根据对 PLA/ SiO_2 , PMMA/ SiO_2 以及 PLA/PMMA/ SiO_2 三种纳米复合材料的 SEM 和流变学实验结果的综合分析, 我们认为 PLA 分子链能够选择性吸附在纳米二氧化硅颗粒周围, 引起 PLA/PMMA 混合物在纳米尺度的局部非均质分布。此外, 流变实验表明纳米二氧化硅的引入提高了 PLA/PMMA 共混物在熔融状态下的粘弹性以及相稳定性, 并且提高了共混物中的链缠结点密度。

关键词: 纳米颗粒; 流变性; 链缠结; 选择性吸附

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Intermolecular cooperativity and entanglement network in a miscible PLA/PMMA blend in the presence of nanosilica

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The effects of nanosilica on the thermo-mechanical and rheological properties of PLA/PMMA 50/50 blends were investigated. It is found that the incorporation of nanosilica does not only increase the glass transition temperature but also extend the broadness of glass transition, attributing to local nanoscale heterogeneities in the miscible blends induced by the self-concentration of the components. According to the results of SEM and rheological measurements, it was proposed that PLA molecules were selectively adsorbed on the surface of nanosilica, and the preferential adsorption of PLA changed the blend composition in the “crater” structure and the bulk matrix. The phase separation temperature of the filled PLA/PMMA blends was also improved by the incorporation of nanosilica, implying a potential role of nanosilica in improving the phase stability of PLA/PMMA blends. In addition, nanosilica could increase the viscoelasticity and entanglement density of PLA/PMMA blends.

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不同极性沥青质对含蜡油胶凝特性的影响

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由于沥青质在原油中特殊的溶解-聚集特性, 即使其含量较低, 仍然是影响含蜡原油流变特性的重要因素^[1~2]。沥青质常被笼统地归类为可溶于苯而不溶于正庚烷的一类物质, 这掩盖了沥青质中各组成之间差异。针对委内瑞拉减压渣油沥青质, 本文采用4种不同比例的溶剂(二氯甲烷:正戊烷), 分离得到极性依次降低的4种沥青质($F_{33/67}$ 、 $F_{25/75}$ 、 $F_{20/80}$ 、 $F_{10/90}$)。分别配制了含蜡量10wt%、沥青质含量0.2wt%的模拟油, 通过分析不同极性沥青质在模拟油中分散程度的差异, 描述了其对含蜡油胶凝温度($G'=G''$ 时对应的温度)的影响。研究表明, 沥青质的存在, 导致含蜡油胶凝温度降低, 且沥青质极性越弱, 降幅越大(图1)。沥青质的极性降低, 其在模拟油中分散程度增大(图2), 小颗粒沥青质对模拟油胶凝产生更强的抑制作用^[1]。

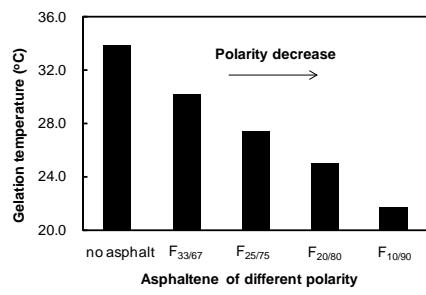


Fig.1 Effect of asphaltenes of different polarity on gelation temperature of model oil

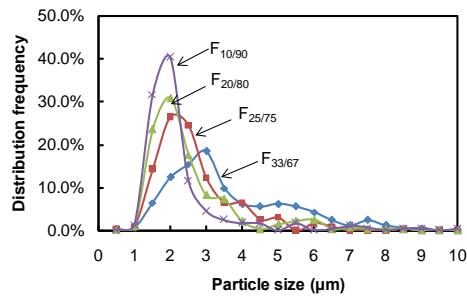


Fig.2 The particle size distribution of asphaltenes of polarity in model oil

关键词: 沥青质; 极性; 分散程度; 胶凝特性

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Effect of Asphaltenes of Different Polarity on Gelation Property of Waxy Oil

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Asphaltene is an important component influencing the rheological properties of waxy crude oil. Generally, the asphaltenes were defined as a solution class that precipitate in heptanes but dissolves in toluene. The changes in polarity for the various components of asphaltene were not highlighted in this definition. In this study, four kinds of asphaltenes of gradually decreasing polarity($F_{33/67}$ 、 $F_{25/75}$ 、 $F_{20/80}$ 、 $F_{10/90}$) were separated from Venezuelan vacuum residue asphaltene using the solvent made of dichloromethane and *n*-pentane at four different volume ratios. The model oils with 10wt% paraffin and 0.2wt% asphaltenes of different polarity were prepared for gelation measurements. The results indicated that the addition of asphaltenes can depress the gelation temperature(T_{gel}) of

model oil. From particle size distribution, the asphaltenes with lower polarity was better dispersed in model oil, resulting in more effective gelation temperature decreasing.

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CNT-g-PDLA 诱导聚乳酸构建立构复合晶体网络

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纳米粒子在聚合物中的空间分布一般通过接枝与基体相同的聚合物实施调控, 但这种方法的难点在于接枝链与基体聚合物没有特殊相互作用[1,2]。本文试图通过PDLA与PLLA之间固有的强相互作用进一步控制CNT的分散状态。结果发现, CNT-g-PDLA填充PLLA体系中, 这种强相互作用不仅可以促进CNT有效分散, 大幅降低渗流导电阈值, 而且沿着CNT表面可以形成PDLA和PLLA立构复合晶体。最惊喜的是, 该立构复合晶体在CNT的诱导下可以形成耐高温的三维网络骨架结构。

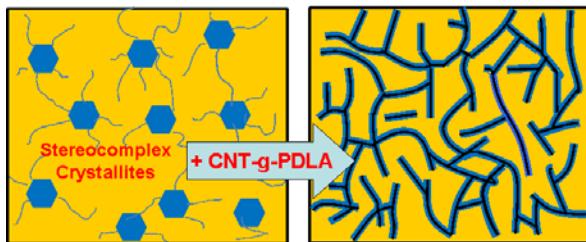


Fig. 1 Schematic diagrams of stereocomplex crystallite (Sc) structure in (a) PLLA/PDLA blends where some Scs may be bridged by polymer chains at high PDLA concentrations and (b) PLLA/CNT-g-PDLA mixtures where Sc forms along the CNT networks.

关键词: 立构复合晶体; 聚乳酸; 纳米碳管; 导电网络

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Forming CNT-Guided Stereocomplex Networks in Polylactide-Based Nanocomposites

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The self-networking structure of poly(D-lactide)-grafted carbon nanotubes (CNT-g-PDLA) in poly(L-lactide) (PLLA) matrix was investigated. Specific interactions between enantiomeric pairs not only promoted CNT dispersion, but also contributed to the regular phase-separation-like CNT self-networking. Furthermore, the grafted PDLA chains preferably formed stable stereocomplex crystallites with the PLLA matrix, and the CNT self-networking resulted in the self-assembly of 3D continuous stereocomplex scaffold. It was demonstrated that the CNT-guided stereocomplex network endows polylactide-based nanocomposites with significantly improved mechanical strength, heat-resistance, and electrical conductivity at low CNT concentrations.

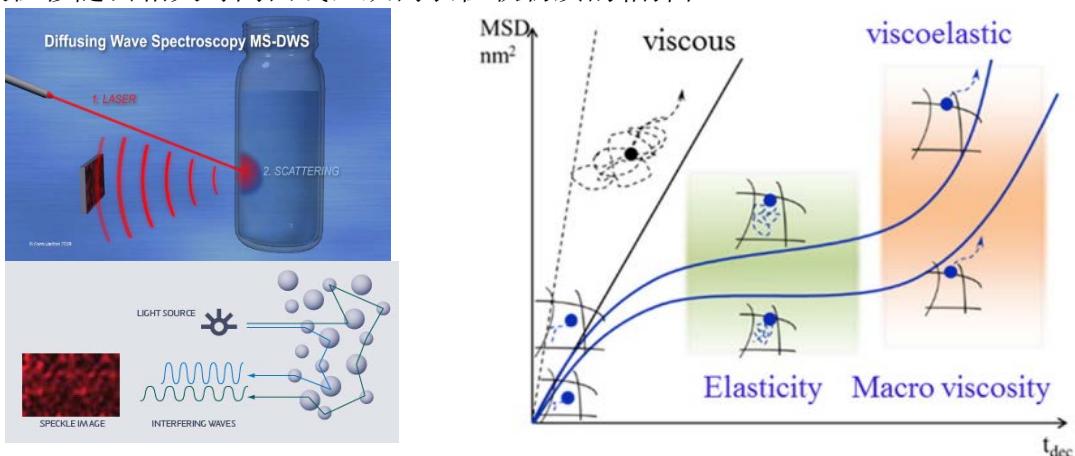
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Rheolaser 微流变仪在软物质流变中的应用

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微流变可以持续追踪微观颗粒的运动位移。微观颗粒的位移直接与软物质的粘弹性相关，颗粒运动速度越快，样品的粘性越低，运动范围越广，样品的弹性越低。目前，可以用来研究颗粒位移的技术有颗粒追踪技术、动态光散射技术和多重光散射技术。在本文中，描述了一个新的测试技术，多散斑扩散光谱 Diffusing Wave Spectroscopy (DWS)，仪器结构如下图左所示，通过 CCD 摄像头检测背散射的相干激光，获取到干涉图像，即散斑图，当颗粒由于布朗运动产生位移时，散斑图会发生改变，通过对大批量的散斑图进行数学去相关处理，获取到颗粒的均方根位移随时间相关曲线，从而表征软物质的粘弹性。



Rheolaser 获取样品的 MSD 曲线代表了样品的粘弹性性质（上图右），纯粘性流体的 MSD 曲线呈直线，带有弹性的样品 MSD 曲线会有明显的弹性平台区（绿色范围），弹性平台区中的 MSD 越靠近下方意味着阻碍颗粒运动的微观网络结构越小，弹性越强；MSD 曲线的后段（橙色范围）体现样品的宏观粘度，该段曲线的斜率越低意味着颗粒在宏观溶剂中的运动速度越慢，粘性越高。

关键词：微流变 均方根位移 DWS MSD

APPLICATION OF RHEOLASER ON SOFT MATERIAL RHEOLOGICAL

Microrheology consists of studying the displacement of microparticles [1]. The displacement is directly related to the viscoelastic properties of a sample. The faster a particles moves, the lower is the sample's viscosity and the wider it moves the lower is the sample's elasticity. To study the particles' displacement, several techniques can be applied, such as particle tracking, dynamic light scattering or multiple light scattering. This work will present a specific technique called Diffusing Wave Spectroscopy (DWS) [1,2,3], in which backscattered light of a coherent LASER is analyzed with a temporal resolution. The backscattered light gives rise to interferential images, so called speckles images, which are detected by a CCD camera. These images change in time due to the Brownian motion of the particles that scatter the light. DWS principle can be applied for bulk and film analyses. Classic DWS microrheology is applied on systems in equilibrium to study the viscoelastic

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准稳态假设对黏塑性流体管道启动流数值模拟影响的研究

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黏塑性流体管道启动流数值模拟中, 为判断屈服面的径向位置, 常在控制方程中引入准稳态假设^[1,2]。但是, 现有文献对准稳态假设的适用条件鲜有深究。本文针对弱可压缩Herschel-Bulkley流体的管道启动流, 借助尺度分析法^[3]对动量方程进行分析, 定义了一个与管道径长比、雷诺数和流动行为指数成正比, 与流体压缩系数和Bingham数成反比的无量纲数 UT 。数值模拟结果显示, 上述五个参数对准稳态假设适用性的影响均可通过 UT 值唯一地体现出来, UT 值越小, 准稳态假设对启动流计算结果的影响越小。 UT 值低于0.065时, 与未采用准稳态假设的计算结果相比, 引入准稳态假设所得末端见流时间的计算偏差在2%以内, 末端流速恢复过程计算偏差在1%以内, 且计算偏差随 UT 减小而减小的速率变缓; UT 值高于0.065时, 准稳态假设使得末端见流时间计算结果显著偏小、流速和压力计算结果的瞬变加剧。

关键词: 黏塑性流体; 准稳态假设; 尺度分析; 启动流

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Effect of quasi-steady assumption on numerical study of start-up flows of weakly compressible Herschel-Bulkley fluid in pipelines

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In the numerical studies of start-up flows of viscoplastic fluids in pipelines, quasi-steady assumption is widely introduced into governing equations to capture the radial position of yield surface. However, there are few studies on the application condition of quasi-steady assumption in existing literatures. In the present work, for the start-up flows of weakly compressible Herschel-Bulkley fluid in pipelines, we define a dimensionless number UT . The numerical studies show that the applicability of quasi-steady assumption depends on and only on the value of UT . With the decreasing of UT , the effect of quasi-steady assumption on simulation results decreases. If $UT < 0.065$, the effect of quasi-steady assumption on simulation results is small; conversely, quasi-steady assumption leads to shorter computed time for the outlet to start to flow, and more drastic computed transient processes of velocities and pressure.

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白炭黑填充羧基丁苯橡胶的多层次微观结构研究

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分别采用悬浮液吸附混合法、胶乳混合并开炼法制备填充份数0~300 phr、0~60 phr的羧基丁苯橡胶/白炭黑(XSBR/A200)复合物, 采用温度调制差示扫描量热法(TMDSC)研究复合物的玻璃化转变行为, 采用动态流变法研究A200的补强机理。TMDSC测试结果显示, “玻璃化层”^[1]含量与填充份数呈线性关系, 且与混合方式无关。流变与TMDSC测试结果对比显示, A200粒子表面存在两层分子能动性不同的受限层, 其中玻璃化层内层不能发生玻璃化转变, “受限外层”^[2]可发生玻璃化转变, 但在高频下呈刚性行为。根据等价球形模型, A200粒子半径为6.8 nm, 玻璃化层与“受限外层”厚度分别为1.0 nm、1.6 nm。

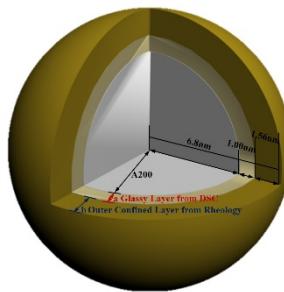


Fig. 1 Schematic diagram of an equivalent A200 nanoparticle of 6.8 nm in radius covered by an inner glassy layer of 1.0 nm in thickness from TMDSC and an outer absorption layer of 1.6 nm from rheology tests

关键词: 羧基丁苯橡胶(XSBR); 纳米二氧化硅; 固定化层; 温度调制差示扫描量热(TMDSC); 流变

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A Study on Multilayer Microstructure of Nanosilica filled Carboxylated Styrene-Butadiene Rubber

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Carboxylated styrene-butadiene rubber/nanosilica (XSBR/A200) composites have been prepared by absorption mixing method (0~300 phr) and latex mixing plus extra open-milling method (0~60 phr). Temperature modulated differential scanning calorimetry (TMDSC) was used to investigate glass-transition behavior of the composites prepared by both methods while dynamic mechanical tests were carried out to investigate the reinforcement of the

compounds prepared by the latex mixing plus extra open-milling methods. TMDSC results show that the content of the glassy layer immobilized in the close vicinity of A200 nanoparticles increases proportionally with silica loading regardless of mixing methods. Comparision between TMDSC and rheology results indicates that there exists an outer absorption layer besides the glassy layer in compounds. The glassy layer corresponds to the XBSR fraction surrounding nanosilica that does not undergo glass transition. On the other hand, the outer layer is able to undergo glass transition together with the bulky rubber phase but it behaves rigid at high frequencies. Both these two layers contribute to the reinforcement effect. Assuming equivalent A200 spheres of 6.8 nm in radius, equivalent thicknesses of the glassy and outer layers are estimated as 1.0 nm and 1.6 nm, respectively.

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无规离聚物物理凝胶行为的边界

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无规离聚物 (Random Ionomer) 是指离子在高分子链上无规分布的一类离聚物。和很多成功的高分子材料一样, 无规离聚物的商业开发也走在了基础研究之前。^{1,2}自从杜邦公司商业化“Surlyn”以来, 离聚物材料已经应用于包装、表面涂膜和记忆材料等多个领域。对于离聚物的结构, 比较经典的模型是Eisenberg的限制区域模型: 由于高分子材料(特别是以碳氢为主体的高分子材料)通常具有较低的极性, 极性的离子基团在高分子基体中会形成聚集。该离子聚集体具有物理交联点的功效, 使得离聚物具有物理凝胶的力学特性。离子聚集会进一步限制周围高分子链段的运动, 受限制的链段随着离子浓度的增加而增加, 进而导致体系玻璃化转变温度的上升。Eisenberg的限制区域模型虽然可以解释离聚物的物理凝胶行为, 但没有回答关于离聚物凝胶的两个基本问题: 凝胶如何在低离子浓度形成而又如何在高离子浓度失效? 对于这两个问题, 我们近期的研究给出了部分答案。凝胶的形成对应的点称为凝胶点, 凝胶点以前, 离子交联会产生尺寸具有一定分布的溶胶, 但没有形成逾渗网络。而达到凝胶点以后, 逾渗网络形成, 且凝胶的比重会随着离子浓度的上升而增加, 使得最终凝胶占据整个体系。我们发现, 凝胶点对应约平均每条链上一个离子的浓度。凝胶形成后, 继续增加离子浓度, 会导致橡胶态模量逐渐增加。最终橡胶态模量与玻璃态模量融合为一个宽分布的松弛过程, 此时凝胶行为失效。我们发现, 该转变对应的离子浓度约为平均每个Kuhn链节上一个离子的浓度。

关键词: 离聚物; 流变学; 线性粘弹性; 物理凝胶

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Boundaries for Ionomer as Reversible Gel

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A random ionomer has ionic groups randomly attached to the polymer backbone. Since Dupont commercialized the first random ionomer under the trade name Surlyn in 1964, the structure and dynamics of random ionomers have been subjected to extensive researches.^{1, 2} Nevertheless, two basic questions have yet to be better understood in respect to ionomer as physical gel: (1) How is the gel formed at low ion content and (2) how does the gel behavior change at high ion content? In our recent studies, we found that (1) the gel point is close to ~ one ion per chain on average and (2) the rubbery and glassy moduli merge at ~ one sticker per Kuhn segment.

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高介电聚合物溶液的流变性能

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导电聚合物是作为一类新型的功能高分子材料，具有独特的超共轭分子结构，拥有许多独特的光、电、磁等功能特性，可广泛用于生物传感器，电磁屏蔽、微纳米制造、有机太阳能电池、有机分子器件等领域。其流变学特性是其能否成功应用的关键。

聚吡咯是导电聚合物的典型代表，它具有合成方便、机械耐受性强、成本低、光电性、热电性、导电性好等优点；与其他超共轭结构的导电聚合物一样，其刚性的共轭链结构导致其不溶不熔难于加工。多年来，研究者一直致力于对聚吡咯及其他共轭聚合物的改性，以期改善其溶解加工性能，近年来的研究进展表明，可溶或者部分可溶的有机导电高分子相继出现。

本文通过化学修饰方法在吡咯环的 N-位分别引入三种不同长度的长链烷基取代基，合成了一系列取代型吡咯衍生物单体。并通过均聚或共聚，合成了系列可溶性聚吡咯衍生物导电聚合物。系统研究了该类导电聚合物溶液的剪切流变行为。揭示了导电聚合物共轭分子结构、柔性结构单元、溶液浓度等对其流变特性的影响，揭示了吡咯基导电聚合物的结构调控与其流变性能调节之间的关系。同时，结合已有研究，系统阐述了具有共轭结构的导电聚合物溶液的流变学研究进展，以及导电聚合物溶液流变性能对其作为有机光电材料应用的重要意义。

SiO₂纳米离子材料组分间相互作用与流变性能的调控

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纳米离子材料(Nanoscale Ionic Materials, NIMs)是聚合物-无机纳米混杂材料的一种特殊形式, 一般由表面经过修饰带上电荷的无机纳米粒子作为内核, 与多个带反电荷的低聚物配对形成[1]。由于纳米离子材料具有类似于离子液体的结构特征, 在没有溶剂的存在下可具有类流体的流动行为[2,3]。本研究中, 以磺酸化的SiO₂纳米粒子(SiO₂-SIT)为内核, 分别与叔胺型、伯氨型或双-NH₂官能团封端的PEO-PPO嵌段共聚物通过酸碱反应配对, 制备出组分间相互作用强度不同的三类纳米离子材料。外层配对离子的结构改变对材料的流变性能产生显著影响。在相同的固含量条件下, 所得材料的动态模量和黏度可以相差几个数量级。在大应变动态测试中, 三种材料也表现出不同的响应行为。

关键词: 纳米离子材料; 离子相互作用; 流变特性; 结构-性能关系

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Tuning of Ionic Interaction and Rheological Properties of SiO₂-based Nanoscale Ionic Materials

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Nanoscale ionic materials (NIMs) are novel organic-inorganic hybrid materials consisting of multi-charged inorganic nanocore that is electrostatically coupled by oppositely charged organic canopy [1]. NIMs can show good fluidity even in the absence of aqueous/organic solvent as they possess some characteristics similar to those of ionic liquids [2, 3]. In this study, the sulfonated SiO₂ nanoparticles were used as the nanocore to prepare three kinds of SiO₂-based NIMs with different ionic interaction strengths between their constituents via acid-base reaction with the low molecular-weight PEO-PPO block copolymers of tertiary amine type, primary amine type or bi-amino-terminated. The structural variations of block copolymers had dramatic influences on the rheological properties of resulted SiO₂-based NIMs. For the materials with the same solid contents, their dynamic shear moduli and viscosities could exhibit several order-of-magnitude difference. Moreover, they showed altered behaviors under the shear of large dynamic strain.

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尼龙 1212/聚乙烯/功能化聚乙烯反应性共混材料流变特性与力学性能相关性研究

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线性低密度聚乙烯接枝马来酸酐 (LLDPE-g-MAH) 和高密度聚乙烯接枝马来酸酐 (HDPE-g-MAH) 作为增容剂, 与尼龙1212和聚乙烯共混制备了尼龙1212/聚乙烯/功能化聚乙烯共混材料, 并对共混材料的力学性能、流变特性和微观形貌进行测定与分析, 研究结果如下: LLDPE-g-MAH和HDPE-g-MAH的加入可以有效增容尼龙1212/聚乙稀共混材料, 并使共混材料的冲击强度明显提高, 共混材料的缺口冲击强度最高可达到92.09kJ/m²。两种共混材料均在测试范围内出现凝胶点, 与凝胶点对应的共混材料的冲击强度均大于其临近点共混材料的冲击强度, 表明尼龙1212/聚乙烯/功能化聚乙烯共混材料流变特性与力学性能具有一定相关性, 流变是确定尼龙1212/聚乙烯/功能化聚乙烯共混材料超韧配方的一种简单、快速、有效的实验方法。

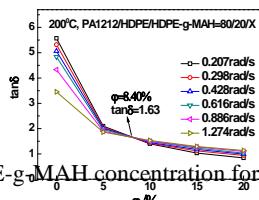


Fig. 1 The relationship between $\tan \delta$ and HDPE-g-MAH concentration for nylon1212/HDPE/HDPE-g-MAH blends at 200°C.

关键词: 尼龙1212; 功能化聚乙烯; 超韧点; 凝胶点

Study on the Relationship between Rheological Characterization and Mechanical Properties of Nylon1212/PE/PE-g-MAH Blends

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HDPE-g-MAH and LLDPE-g-MAH as compatibilizers had been blended with nylon 1212 and polyethylene and prepared nylon 1212/PE/PE-g-MAH blends. The rheological characterization, mechanical properties and morphologies of blends had been investigated. Two compatibilizers can improve the compatibility of nylon1212/PE blends, and increase greatly the toughness of blends. The highest impact strength of blends attained to 92.09 kJ/m². Both of the blends exhibited obvious “gel points” in the test range, and the impact strength of blends corresponding to gel point were significantly greater than the near point. These results indicated the “gel points” acquired from the dynamic rheological data and the “super-toughness points”of the blends had a corresponding relationship. Thus, just by simple composition designs and a small amount of samples, the super-toughness point could be conveniently determined by the dynamic rheological measurements.

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纳米粒子对 PS/PVME 共混物粘弹相分离动力学和机理的影响

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高分子材料多为共混/复合的多相体系, 其性能取决于共混物的形态与结构, 故高分子共混体系的相行为一直为人们所关注。而纳米粒子填充共混物可在改善聚合物基体的力学性能的基础上赋予材料新的功能, 还可以有效调控共混物基体的相分离行为。通常, 基于相分离过程中扩散、粘弹性以及流体力学力三个方面考虑, 引入纳米粒子可以改变链段松弛行为、两相粘弹性差异以及界面张力, 从而对相分离行为进行调控^[1-4]。对于聚苯乙烯/聚甲基乙烯基醚(PS/PVME)体系中, PS 较小的偶极矩使其对介电松弛强度的贡献相较于 PVME 可以忽略, 因此我们可借助介电松弛谱研究共混和复合体系中不同相分离阶段 PVME 的松弛行为变化。基于均相共混物动力学异质的特点, PVME 的松弛行为决定于其局部环境, 即其在共混物中的组成, 我们将不同阶段 PVME 松弛行为的变化与其组成的变化关联, 可以获得纳米粒子在相分离过程中对体系组成变化的影响。

关键词: 聚合物共混物; 粘弹相分离; 纳米粒子

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Effect of Nanoparticles on the Kinetics and Mechanism of Viscoelastic Phase Separation for PS/PVME Blend

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The incorporation of nanoparticles into polymer blends may improve their mechanical properties and endow the materials new functions, as well as control the morphology and phase separation behavior of blend matrix effectively. Polystyrene/poly(vinyl methyl ether)(PS/PVME) blend is the most well studied polymer mixtures as regards phase separation and dynamic heterogeneous due to its negligible contribution to dielectric loss for PS molecular motion. We investigated the evolution of PVME relaxation by dielectric spectrum of the blends and nanocomposites after being annealed for different time above the phase separation temperature and then attained the influence of nanoparticles on the composition variation of blend matrix during phase separation.

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热塑性聚氨酯流变行为的研究 *

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采用预聚体法本体聚合, 以聚己内酯二醇(PCL)、4, 4'-二苯基甲烷二异氰酸酯(4, 4'-MDI)和1, 4-丁二醇(1, 4-BDO)制备热塑性聚氨酯弹性体(TPUE)。通过DSC和流变测试研究热塑性聚氨酯在其熔点附近的流变行为。热塑性聚氨酯弹性体以硬段微区作为物理交联点起到物理交联作用。流变结果显示, 在对样品进行动态频率扫描时样品储存模量G'在低频区出现平台, 即低频区弹性增加。对同一样品连续重复进行动态频率扫描, 发现G'较前一次频率扫描增大, 且增加幅度随测试温度增加出现峰值。动态时间扫描也可以发现TPUE的G'在测试过程中呈不断上升的趋势, 且上升幅度同样随测试温度的上升出现峰值, 当测试温度超过TPUE硬段熔融温度后G'不随测试时间变化而改变。DSC测试表明, TPUE硬段熔融温度(T_m)与流变频率扫描中G'增幅最大时的测试温度相对应, 当降低可结晶的硬段组分含量后, G'上升的趋势明显减缓, 流变测试中出现的现象应与TPU的硬段结晶行为有关。

关键词: 热塑性聚氨酯; 流变; 结晶

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Rheological characterization of thermoplastic polyurethane elastomer

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Thermoplastic polyurethane elastomer (TPUE) are prepared by poly-caprolactone glycol (PCL), diphenylmethane-4,4'-diisocyanate (4,4-MDI) and 1,4-butanediol (1,4-BDO).The hard segments of TPUE form hard microdomains which play the role of physical crosslink. The rheological dates of frequency and time test show that the storage modulus (G') have a increasement with increasing time. The G' increases during repeating frequency sweep and the increasement of G' have a peak with the increasing temperature which approach to melt point measured by DSC. The paltform at low frequency disappears when temperature over melt point. When we decrease the content of hard segment in TPUE, the incresement of G' weaken. It is related to temperature and content of hard segments. The crystallization of hard segments cause this rheological phonomenon.

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流变学-拉曼光谱联用在聚合物研究中的优势

关键词：流变学，拉曼光谱，聚合物

报告人：Stephen. Sun.

作者：Anthony Kotula, Angela Hight Walker, Kalman Migler (NIST) Matthew Meyer, Francesca de Vito, Jan Plog;

引言

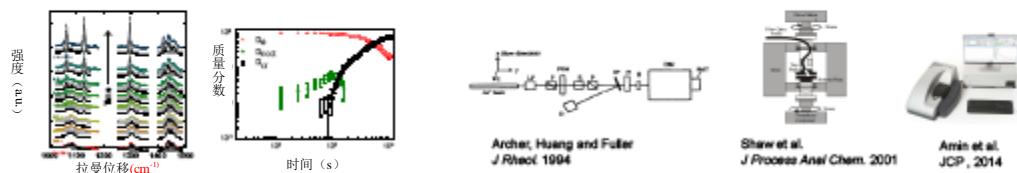
为何将流变学、拉曼光谱学和光学显微术相结合？

流变学可全面阐述试样粘弹性，但无法直接提供分子级信息。

拉曼光谱学可检测分子构型、化学性质、分子取向及纳米结构的变化。

光学显微术揭示与上述方法相关的微观结构。

对瞬态现象的研究需采用同步测定技术

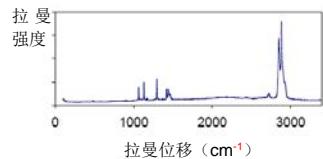


现有研究：通过拉曼光谱得到的结晶动力学数据 现有流变学与拉曼技术结合

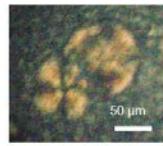
Rheo-Raman 显微镜

- | 拉曼光谱法 | 偏振反射显微法 | 剪切流变学 |
|-------------------------------|--------------------------------------|----------------------------|
| ● 激光: 532 nm 或 780 nm | ● 样品直接成像 | ● 应力控制式流变仪 |
| ● 光谱分辨率: 2-5 cm ⁻¹ | ● 对双折射结构灵敏(长度标度, 单位: μm) | ● 常用粘弹性参数(粘度、复数剪切模量和蠕变柔量等) |
| ● 圆偏振光, 减少偏振/取向效应 | | ● 对力学变化的影响(受链排列和结晶度的影响) |
| ● 对化学性质、分子链构象和结晶度灵敏 | | |

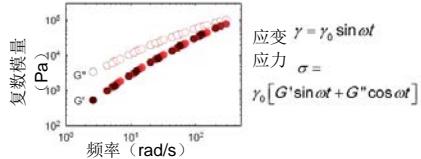
SRM 1475 拉曼光谱



球晶体



熔体流变学



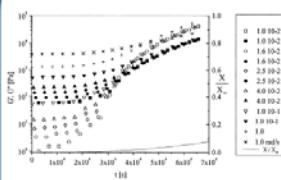
流变仪测量头含玻璃底板、可移动物镜(促进拉曼光谱学、流变学和成像的整合)。



Rheo-Raman 显微镜安装团队!

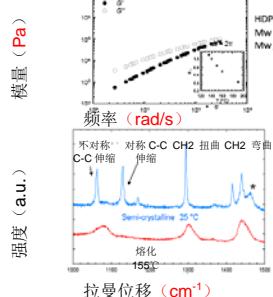
(顶视图、底座)
拉曼和反射显微法所用物镜可从样品中心移至外缘。

案例研究 I: 聚合物结晶 (HDPE)

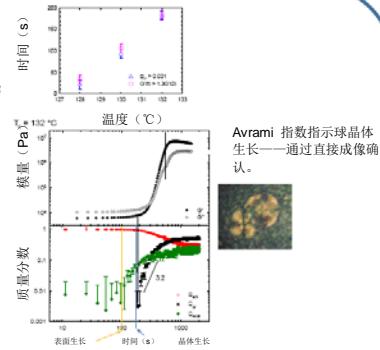


Pogodina; Winter;
macromolecules
1998, 31, 8164-8172.

现有研究 (如 Winter 等人的研究)
先对模量变化进行测量, 后调用模
型来估计相应结晶度。



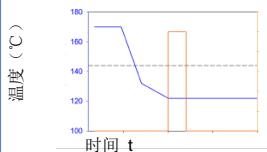
首先在固定温度条件下测定流变学
和拉曼光谱。



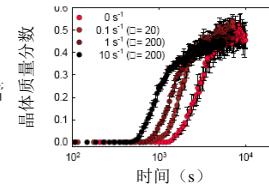
Avrami 指数指示球晶体
生长——通过直接成像确
认。

将拉曼和小振幅剪切 (SAOS) 结合后,
可单独测量模量和结晶度。

案例研究 II: 流动致结晶

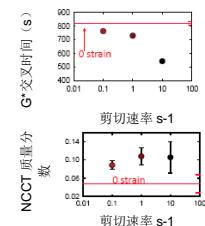


HDPE SRM 1475;
Mw 53.1 kg/mol
Mw/Mn = 2.9



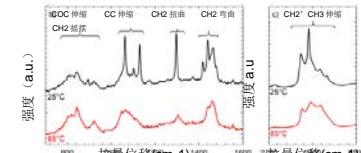
在案例 I 中, 我们将切变 (SAOS) 用
作结晶度的探针; 但我们还可用切变引导
或修正 (结晶) 转化。

在冷却过程中, 切变脉冲的影响在结晶动
力学开始时就能够清晰观察到。最终结晶
度几乎不受影响。



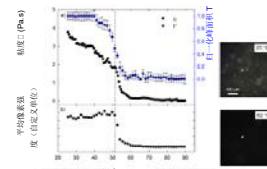
我们可对比不同的力学特性和构象特性
(作为切变脉冲振幅的函数)。

案例研究 III: 化妆品乳化剂



配方包括 20 多种组分, 难以精确定位稳
定性或流变转换的起因。

固定温度条件下所测定的拉曼光谱结果表
明反式构象的 CH₂ 基团会随着温度升高
而熔化。



同步测量结果表明, 熔化行为源于椰子和
杏仁油上的烷基链

前景

由于流变特性与物质的化学、构象或结构
性质密切相关, 因此, 拉曼与流变联用技
术可用于软物质系统的分析。还可用于温
度或流量引起的转换及非线性流变学。

热塑性 (迄今为止)

- 聚乙烯
- 聚丙烯
- 聚己酸内酯
- 聚氨酯

应用:

- 光敏聚合物
- 复合材料
- 生物聚合物
- 反应性共混物
- 链烷烃

未来升级:

- 偏振拉曼
- 紫外光固化
- 应变成像

吡咯基导电聚合物纳米颗粒分散体系流变性能研究

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摘要：聚合物纳米颗粒因其具有独特的性能而得到广泛研究；但对聚合物纳米颗粒分散体系的流变学研究仍有空白。通过流变性能变化反推纳米颗粒粒径和形貌在外力场作用下的变化以及流变参数对其形貌的影响值得研究。本研究首先通过吡咯与二溴乙烷在碱性条件下的亲核取代反应以及之后的消除反应，制得了 N-乙烯基吡咯单体。在 PVP 作为稳定剂、H₂O₂ 作为氧化剂、紫外光催化下的水介质体系中，单体 N-乙烯基吡咯自由基微乳液聚合，形成以水为分散介质的聚 N-乙烯基吡咯纳米颗粒分散体系。在配置一系列浓度梯度分散液后，利用旋转流变仪，研究不同剪切速率下，分散体系不同浓度、不同温度以及不同粒径分布对体系表观粘度的变化；同时采用近似方法制备聚吡咯纳米颗粒及其分散体系，系统研究其流变性能；从而研究了导电聚合物聚吡咯及其衍生物纳米颗粒分散体系的流变学性质及其规律。

高强度聚离子复合物水凝胶的制备及其加工性能研究

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高强度水凝胶由于其优异的力学性能在软材料领域引起了广泛的注意,但是通过化学键交联制备的高强水凝胶如双网络水凝胶往往具有较差的加工性,这极大地限制了这类材料在实际应生活中的使用^[1]。因此,本文介绍一种聚离子复合体(PIC)水凝胶,这种水凝胶完全由离子键交联,它不仅具有出色的机械性能(拉伸强度约3.7MPa,断裂伸长率达到700%,撕裂能达到8000J/m²),而且由于其中的离子键的强度能够通过加入盐水的浓度来调控,使得这种材料能够通过模压、挤出等加工方式制备具有特定形状的水凝胶^[2]。在纯水中浸泡后,凝胶中的小分子盐以及对离子扩散出来,离子键恢复强度,得到高强度的水凝胶。其次,由于离子键的动态可逆性,这种水凝胶还表现出出色的自回复、修复性能。这种具有可加工性能的高强度水凝胶将有望应用于在软体机器人和组织工程等领域。

关键词: 高强度水凝胶; 聚离子复合物; 超分子水凝胶; 加工性

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Preparation of Tough Polyion Complex Hydrogels and Their Processibility

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Tough hydrogels have attracted have received increasing attentions due to its excellent mechanical properties. However, tough hydrogels often have poor processibility, which greatly limits its practical applications. We introduced here processing a tough hydrogel, which is completely crosslinked by ionic bonds. This polyionic complex (PIC) hydrogel possesses excellent mechanical properties, with tensile fracture stress, fracture strain and tearing fracture energy being 3.7 MPa, 700% and 8000 J/m², respectively. Moreover, the strength of the ionic bonds can be effectively tuned by saline solution with selected concentration, making it possible to process this hydrogel by normal processing methods like compression moulding or extruding. This PIC hydrogel also exhibits stimuli-triggered healing properties owing to the dynamic and reversible nature of the ionic bonds. This study should promote the applications of tough PIC gels in structural elements of soft actuators and artificial organs.

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PA1212/POE/POE-g-MAH 共混材料的力学性能与流变特性相关性研究

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通过熔融共混的方法制备了组成不同的PA1212/POE/POE-g-MAH三元共混合金材料, 并对共混材料的力学性能和流变特性进行测定与分析。结果表明, 三元共混合金材料在所研究的测试范围内出现明显的凝胶点, 对应于凝胶点组成(PA1212/POE/POE-g-MAH的质量比为80/13/7)的共混材料韧性最好, 缺口冲击强度达到84.79 kJ/m², 是纯尼龙1212的5.2倍。这表明共混材料的力学性能与流变特性具有一定的相关性, 流变学是确定尼龙1212超韧材料配方的一种简单、快速、有效的实验方法。

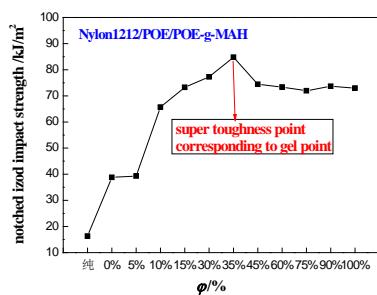


Fig. 1 Relationship between NIIS of nylon1212/POE/POE-g-MAH blends and POE-g-MAH concentration.

关键词: 超韧尼龙; 流变学; 力学性能; 凝胶点

Study on the Relationship between Mechanical Property and Rheological Characterization of PA1212/POE/POE-g-MAH Blends

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We had prepared PA1212/POE/POE-g-MAH blends by reactive blending and investigated their mechanical properties and rheological behavior. The rheological curves of blends shows an obvious “gel point”, the blend (80/13/7) corresponding to the gel point has higher notched izod impact strength than those of other blends. The results indicated the “gel points” acquired from the dynamic rheological data and the “super-toughness points” of the blends have a corresponding relationship. Thus, just by simple composition designs and a small amount of samples, the super-toughness point could be conveniently determined by the dynamic rheological measurements.

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压裂液稠化剂分子结构对支撑剂沉降能力影响

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摘要: 本文以羟丙基瓜胶、水溶性纤维素、高分子聚合物三种压裂液稠化剂为研究对象, 利用不同试验手段分析了交联和不交联压裂液的微观结构, 比较了分子结构与压裂液粘弹性、减阻效果及携砂能力的关系。其中, 支撑剂单颗粒沉降速率都随着粘弹性模量的增大而减小。羟丙基瓜胶和纤维素线性胶, 以粘性为主, 耐高温聚合物线性胶粘弹性相当, 此3种液体中单颗粒支撑剂沉降速率与复模量 G*拟合相关系数很高, 当粘度大于 7.63mPa·s 时, 粘度可以作为体系间近似的比较依据; 聚合物液体内部非常密集的片层结构相互连接, 使液体粘性和弹性增加; 羟丙基瓜胶和纤维素液体内部为疏松的片层结构, 线性结构纤维素液体减阻效果突出, 网状结构交联羟丙基瓜胶压裂液携砂能力强。

关键词: 分子结构, 粘弹性, 沉降速率, 抗剪切, 减阻, 携砂能力

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硫化橡胶动态网络与固相回收

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目前全世界每年橡胶的生产和消费量快速增加,由此也产生大量的废旧橡胶。这些废旧橡胶不仅给环境带来沉重的负担,而且还浪费了宝贵的橡胶资源。目前废旧橡胶的回收利用主要是依靠在橡胶回收过程中添加橡胶再生剂、硫化剂或促进剂等化学手段或者利用超声、微波、高温高压等物理手段进行脱硫回收,回收过程较为复杂,耗能较大,条件苛刻。

事实上,硫化橡胶的分子结构是由线形的橡胶大分子链与硫磺及促进剂等交联反应而形成的三维网络结构,其交联键由单硫键、双硫键和多硫键等组成,而双硫键具有动态可逆交换的特性。本工作致力于有效促进硫化橡胶体系中动态可逆二硫键发生交换反应,从而实现硫化橡胶交联网络的重组,最终赋予硫化橡胶自修复和可固相回收能力,方法简便,不仅可以延长硫化橡胶的使用寿命,还可以减少环境污染,节约橡胶资源,对于传统高分子材料智能化具有重要意义。

荧光素改性层状双金属氢氧化物在橡胶基体中的三维结构示踪 *

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Payne效应是研究填充橡胶材料动态行为的重要窗口, 其机理之一为填料聚集体的团聚-解聚行为^[1,2]。普通光学显微镜较低的分辨率以及电子显微镜受限的操作环境导致填料在不同应变下的结构变化难以被观察到^[3]。本工作利用荧光素钠与层状双金属氢氧化物(LDH)的静电作用制备出荧光改性的微米级和纳米级LDH, 通过溶液共混令填料均匀分散于橡胶基体。利用激光共聚焦显微镜(LSCM)观察LDH聚集体在不同应变下的结构变化, 实现了填料在橡胶基体中的实时观察。采用透射电子显微镜、旋转流变仪、示差扫描量热计等测试将粒子聚集体的形态变化与填充橡胶的流变行为结合起来, 结果表明低填充下橡胶的Payne效应主要来源于基体分子链解缠结, 微米级LDH可促进分子链解缠结, 增强体系Payne效应幅度。

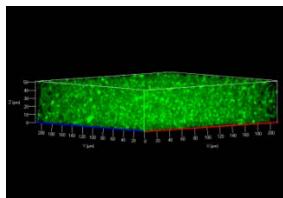


Fig. 1 LSCM image of rubber filled with the fluorescein modified LDH microsheets at the loadings of 10 wt%.

关键词: 层状双金属氢氧化物; 荧光; 流变行为; Payne效应

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Revealing the three-dimensional filler structure in rubber matrix based on a fluorescein modified layered double hydroxide

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Payne effect with the general concept that comes from the filler agglomeration-deagglomeration, is an important window to study the dynamic behavior of filled rubber materials. It is a fundamental challenge to characterize the filler structure under different strains due to the low resolution of optical microscope and the limited operating environment of electron microscope. In this work, fluorescein modified layered double hydroxides were uniformly introduced into the rubber matrix through solution blending method, and laser scanning confocal microscopy (LSCM) was employed to monitor the filler structure under different strains. Based on the results including transmission electron microscope, rheometer and differential scanning calorimetry, the primary mechanism for Payne effect in this system is mainly associated with the entanglement network in rubber matrix, and LDH microsheets could enhance the Payne effect.

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新型磁流变弹性体的制备及表征

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磁流变弹性体(MRE)属于一种新型的智能颗粒增强弹性体,是将微米级磁性颗粒分散到聚合物基体中固化而成。通过改变外加的磁场强度,磁流变弹性体的模量、阻尼等性能能够得到实时可逆的控制,在隔振缓冲、磁控传感等领域具有广阔的应用前景。本文主要介绍了从基体、界面和颗粒三方面对磁流变弹性体做出的材料改进研究,并阐述了这种新型MRE的应用背景。首先基体方面通过制备聚氨酯/环氧树脂互穿网络结构基体提高了MRE的力学强度和阻尼特性,其SEM图及内部结构示意图如图一所示。

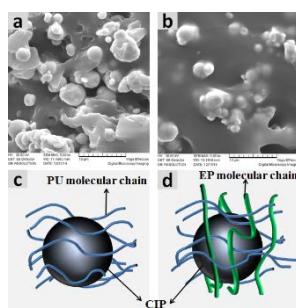


Fig 1. The SEM images and sketches of interface between the CIP and matrix of MRE samples.
其次在界面方面通过在羧基铁粉表面镀上一层纳米铁提高了磁流变弹性体的磁流变效应及阻尼特性, 颗粒表面结构如图二所示。

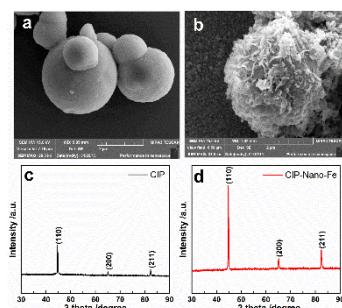


Fig 2. The SEM and XRD of CI particles before and after coated with Fe nanostructures
最后在颗粒方面利用硬磁颗粒NdFeB替代传统MRE中的软磁颗粒,实现了MRE的双向磁控刚度特性,如图三所示。

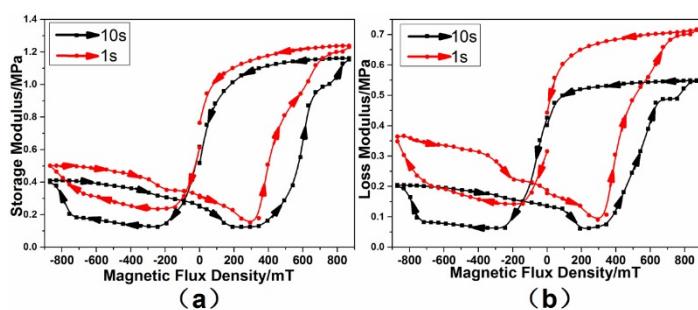


Fig 2. Field dependences of the modulus for MRE under different rate of magnetic field change.
研制出的具有高力学特性、高阻尼且具有双向磁控刚度特性的MRE在智能减震领域拥有巨大潜

力。

关键词：磁流变弹性体；互穿网络结构；纳米铁；双向磁控刚度

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Material Preparation and Characterization of novel Magnetorheological Elastomers

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Magnetorheological elastomers (MREs) are well-known smart particle reinforced elastomer, which consisting of micronized magnetic particles suspended in an elastic matrix. MRE has excellent magnetic-control mechanical properties, and it brought broad prospects of application in the fields of noise reduction, vibration attenuation and smart sensing. This paper mainly introduced the material researches of MRE which focus on the improvement of matrix, interface and magnetic-particle. In the study of the matrix, we prepared a MRE based on polyurethane /epoxy interpenetrating network structure matrix, and the damping and mechanical properties of this MRE were improved. In interface research, Fe nano-flakes coated carbonyl iron particles were prepared to improve the damping property and magnetorheological effect. For the magnetic-particle, we replaced the soft magnetism particles by NdFeB particles. The novel MRE was showed a bi-directional magnetic-control modulus. The MRE with high damping, high strength and bi-directional magnetic-control modulus would offer promising advantages in seismologic application.

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明胶盐溶液物理凝胶化的流变学研究

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明胶水凝胶作为一种蛋白质凝胶, 被广泛的应用于食品及医药等领域。明胶的物理凝胶化伴随着大分子链的构象从无规线团到三股螺旋 (random coils-triple helices) 的转变, 盐的加入将在一定程度上影响到蛋白质分子的构象转变。本文系统地研究了盐的种类及浓度对聚合物物理凝胶化温度以及凝胶粘弹性的影响。结果发现在相同盐浓度的条件下, 聚合物凝胶化温度变化的趋势遵循 $\text{CrCl}_3 > \text{CaCl}_2 > \text{NaCl}$, 而凝胶储能模量的变化趋势则相反; 另外, 明胶的凝胶化温度随 NaCl 浓度的增加先升高后降低 (图 1); 此外, 基于 Hofmeister 效应, 考察了不同阴离子对明胶物理凝胶化温度以及凝胶流变性能的影响。通过上述研究, 将有助于阐明蛋白质分子与反离子间的相互作用机理, 实现复杂体系中聚电解质凝胶结构的调控, 为蛋白质基材料的应用提供有价值的理论指导。

关键词: 聚电解质; 物理凝胶; 粘弹性

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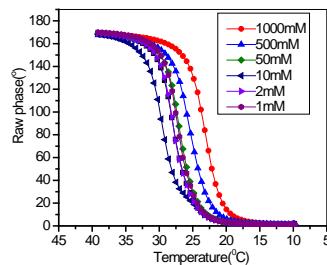


Fig. 1 The temperature dependence of Raw phase of gelatin in NaCl solutions with different concentrations

The physical gelation of gelatin in salt solutions: rheology study

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A series of physically cross-linked gelatin networks with and without salts (NaCl , CaCl_2 and CrCl_3) were prepared. It was found that the gelation temperature increased with an increase in valence of cations. However, the opposite trend was observed in respect of the storage modulus of gels. Moreover, the influences of the anions on the gelation temperature and rheological behaviors of gelatin composite gels were studied in detail.

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凝胶过程微流变学研究^{**}

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摘要:稠化剂凝胶化过程对压裂成功十分重要。本文应用光学微流变仪研究了不同稠化剂溶液凝胶化过程的微流变学性质。考察了稠化剂和交联剂浓度、交联温度等对凝胶化过程微流变学性质(如弹性因子等)的影响,获得了凝胶化过程中弹性因子随时间的变化曲线。应用4-参数本征交联流变动力学方程确切表征稠化剂溶液交联凝胶化过程中弹性因子变化曲线。说明微流变学是研究稠化剂溶液交联凝胶化本征流变动力学的有效方法。

关键词:微流变, 凝胶过程, 流变动力学; 压裂液

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Microrheology on Gelation Process

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The gelation process of fracturing thickener solution is very important for success of fracturing operations. The microrheological properties on gel formation processes of different thickeners solutions have been studied with optical microrheometer. The effects of concentrations of thickeners solution and crosslinking agent, temperature on the microrheological properties (such as Elastic Index, etc.) during gelation process were investigated. The Elastic Index (EI) curves during gelation processes for different thickeners solutions were obtained. A 4-parameter intrinsic rheokinetics equation was applied to describe the EI curves during cross-linking gel formation process of thickeners solutions correctly. It is proved that microrheology is useful to study the intrinsic rheokinetics of static crosslinking process of thickener solution.

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熔体加工中原位微纤化的流变学因素

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熔体加工过程中发生原位微纤化是增强不相容共混物的高效方法, 在学术研究及工业应用领域都引起了广泛兴趣。我们近期的研究将两种新型的不相容共混物(PP/PLA和OBC/PP)成功制成微纤增强复合材料(MFCs), 其中分散相组分形成了结构精细、高长径比、尺寸为微米/纳米级的微纤, 并且系统研究了链结构、相互作用、粘度比、剪切速率(转速)、拉伸比、熔体受限程度等组分、流变及加工条件因素对所获得微纤化形态的影响。对比研究发现组分间粘度比及熔体受限流动这两种流变学因素对微纤化形态是最重要的。除了显著的力学增强和热稳定性提高外, 通过引入纳米填料(CNTs)还能够赋予MFCs材料新的功能, 如优良的导电性能。

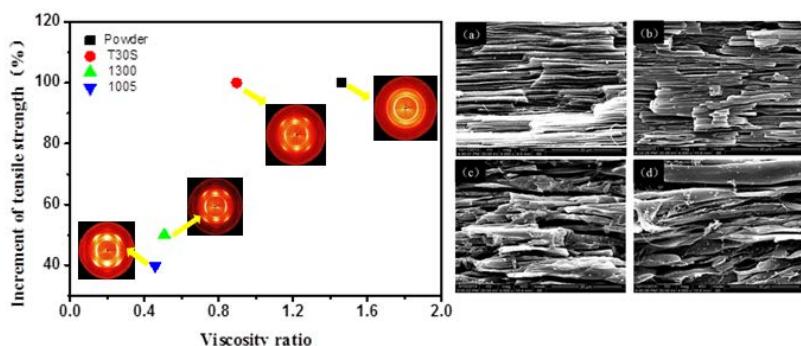


Fig. 1 Correlation of viscosity ratio and microfibrillar morphology in the MFCs of PP/PLA

关键词: 不相容共混物; 原位微纤化; 粘度比; 受限流动

Rheological effects on the in-situ microfibrillation during melt processing

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Recently, the microfibrillation of immiscible blends during melt processing has attracted extensive attentions in both academic and industrial fields, due to as an effective method for mechanical reinforcement. In this presentation, two kinds of newly developed immiscible blend were fabricated into microfiber-reinforced composites (MFCs) successfully, in which the dispersed-phase components formed into well-defined microfibrillar entities with high aspect ratio and micro-/nano-scale size. Many factors, such as chain architecture, interaction, viscosity ratio, shear rate, extension degree, confinement of melt flow, are addressed systematically to access their importances on formation of microfibrillar morphology. It is interesting to suggest that two rheological effects, viscosity ratio and confinement of melt flow, play essential role on microfibrillar morphology. Excellent mechanical strengthening and thermal stability were achieved in the MFCs prepared.

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地面交联酸流变性能研究

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酸化压裂改造技术是碳酸盐岩储层和裂缝性砂岩储层增产改造的主导技术, 地面交联酸是一种新型的适用于酸化压裂的压裂液体系, 但是目前关于地面交联酸体系交联反应特征、耐剪切性能, 以及影响因素的研究还不够深入。文中以酚醛树脂和合成有机锆作为交联剂, 以盐酸质量分数为 20%的稠化剂溶液作为基液, 对这两种的地面交联酸体系分别进行了流变学研究, 测定了这两种体系在不同交联比下的耐温耐剪切性能, 交联过程黏弹性模量随时间的变化, 以及不同剪切速率和不同温度下的流变曲线, 讨论了交联比、温度、剪切速率对交联反应的影响。并对酚醛树脂和有机锆交联体系进行了对比和分析。研究地面交联酸的流变性质, 对于交联酸体系的研发和改进十分重要。

关键词: 地面交联酸; 流变学; 酸化压裂

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Rheological Property Study of In-situ Crosslinked Acid Gel

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Fracture acidizing has been used as a key way to boost production for carbonate reservoir and sandstone reservoir. in-situ crosslinked acid gel is a new fluid developed for fracture acidizing. The study for it is not specific however, especially for shear properties, characteristic of crosslinking, and influence factors. Two kinds of gel was studied, which has different crosslinking agent and same polymer solution. phenolic emulsions and organic zirconium are different crosslinking agent, and polymer solution contains 20%(wt)HCl. The shear properties in different Crosslinking ratio, and the changes of viscosity and viscoelastic modulus with time was tested both of the two system. As well as the Rheological curve of under the different shear rates and different temperature. The influence of the Crosslinking ratio, temperature, and shear rates to gel was also investigated at the conclusion. This study is very important for the research of in-situ crosslinked acid gel.

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多糖水凝胶和多糖乳化液的流变学性质

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多糖是一类具有特殊化学结构、复杂分子构象和流变学特性的天然大分子。多糖的生物活性、生理功能、对健康的促进作用、增粘和凝胶化等流变学特性、乳化特性、物理的和化学的改性、各类交联方式形成的水凝胶材料的开发一直是多糖研究的主要内容。多糖水凝胶和多糖乳化剂在材料、医药、食品、化妆品和化工等领域有广泛而重要的应用。许多多糖都具有一经发现即迅速形成工业化应用的特点，这些多糖包括透明质酸、结冷胶、可德胶（可得然胶）、黄原胶、果胶、魔芋葡甘露聚糖、阿拉伯胶、玉米纤维胶、大豆多糖和海藻酸盐等。它们有的是近年开发的，有些则已被人类应用了数千年。

基于应力和形变关系研究的流变学是多糖水凝胶材料和多糖乳化作用研究中的重要表征手段。水凝胶是用途广泛的功能性软物质。具有形成水凝胶的能力是许多多糖最重要的特性，也是多糖利用的一个最重要方面。很多多糖是水凝胶材料的制备来源。多糖的凝胶化性质在生物医药、食品和化工等诸多领域发挥着重要的作用。多糖水凝胶材料在组织工程、细胞固定、药物包敷、食品质地改良和风味释放、化工产品物理性能控制等许多方面有重要的应用。具有乳化特性是一些多糖的又一重要特性，而具有乳化特性的多糖又有着独特的流变学，特别是界面流变学性质。流变学作为多糖水凝胶研究中不可或缺的手段，也是多糖乳化特性研究的重要工具。本文以流变学研究为纽带，着重阐述了多种多糖独特的本体和界面流变学性质。

关键词：多糖；水凝胶；乳化；流变学

Rheological properties of hydrogels and emulsions of polysaccharides

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Polysaccharides are natural polymers with special structures, complex conformation and rheological properties. A lot of polysaccharides have shown unique gelling abilities to form hydrogels with saliently rheological features, and emulsifications with interfacial films of different viscoelasticities. Rheological method has been shown a powerful tool to characterize polysaccharide hydrogels and emulsifiers. In the present work we emphasize the bulk and interfacial rheological behavior of several typical polysaccharides.

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持续升温时稀疏 CTAC 表面活性剂溶液剪切黏度变化的动力及能量分析

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摘要: 在恒定的剪切速率下、持续升温, 对稀疏CTAC/NaSal表面活性剂溶液进行流变测试, 发现不同剪切速率下, 即便升温速度相同, 同一溶液内分子自组装结构变化的差异也很大。首次发现“双峰”现象, 其形成条件为: 溶液浓度1.25-2.50 mmol/L、剪切速率5 s⁻¹、升温速度0.0033-0.0333 °C/s。建立了棒状胶束尺寸变化速度与温度和剪切速率之间的关系式(见下图), 可以发现不管是剪切还是温度, 对胶束尺寸变化的作用都具有两面性, 因此, 试验条件下胶束尺寸大小实际上取决于剪切和温度两种作用的“匹配程度”。此外, 引进总自由能变的概念, 从能量角度分析了剪切和温度对表面活性剂胶束溶液的协同作用。

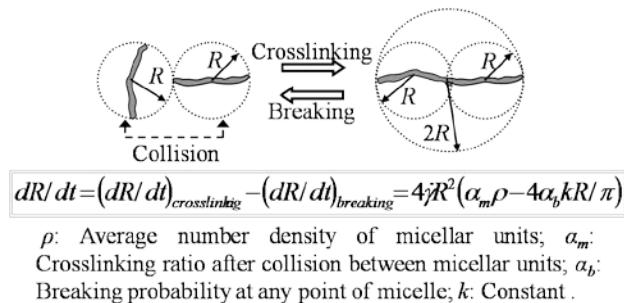


Fig. 1 Relation between the change in rodlike micelle size with time (dR/dt) and the combined effects of shear and temperature

关键词: 表面活性剂; 稀疏; 自组装结构转变; “双峰”现象; 总自由能变

Dynamic and Energy Analysis on the Viscosity Transitions with Increasing Temperature under Shear for Dilute CTAC Surfactant Solutions

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ABSTRACT: Quite dilute CTAC/NaSal surfactant solution has been investigated with increasing temperature under shear. Different shear rates induce very different assembly transitions for the same solution with same temperature increasing rate (r). A special “two peaks” phenomenon appears under the following conditions: concentration of 1.25-2.50 mmol/l, shear rate of 5 s⁻¹ and r of 0.0033-0.0333 °C/s. An equation is established to describe the relations between the change in rodlike micelle size with time (dR/dt) and the combined effects of shear and temperature. It can be found that either effect of shear or temperature has two aspects on dR/dt , therefore, the micellar size actually depends on the “matching-degree” of the two effects under our experimental conditions. Besides, the total free energy change in the surfactant solution system is analyzed to study the simultaneous effects of shear and temperature from energy viewpoint.

Keywords: surfactant; dilute; self-assembly transition; “two peaks” phenomenon; total free energy change

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PA1212/功能化聚丙烯共混材料流变特性与力学性能相关性研究

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通过熔融接枝的方法制备了马来酸酐接枝聚丙烯(PP-g-MAH),与PA1212共混制备了PA1212/PP-g-MAH反应性共混材料,考察了PP-g-MAH的含量和接枝率对共混材料力学性能及流变特性的影响。结果表明,接枝率不同的PP-g-MAH的加入能够显著提高PA1212的冲击强度。两种共混材料均在测试范围内出现一个凝胶点,与凝胶点处相对应的尼龙1212/PP-g-MAH共混材料的冲击强度明显大于其临近点共混材料的冲击强度。表明尼龙1212/功能化聚丙烯共混材料流变特性与力学性能具有一定相关性,流变是确定尼龙1212/功能化聚丙烯共混材料超韧配方的一种简单、快速、有效的实验方法。

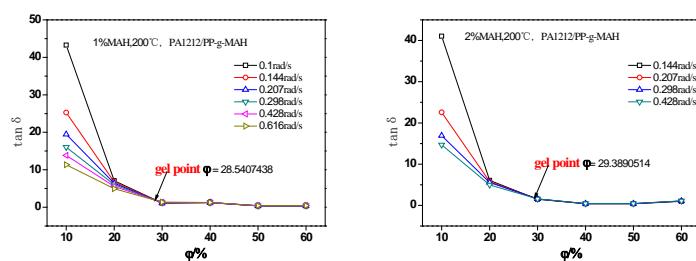


Fig. 1 The relationship between $\tan \delta$ and PP-g-MAH concentration for nylon1212/PP-g-MAH blends at 200°C.

关键词：功能化聚丙烯；反应性共混；凝胶点；流变学

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Study on the Relationship between Mechanical Property and Rheological Characterization of PA1212/PP-g-MAH Blends

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PP-g-MAH had been prepared by melt grafting method, and blended with PA1212 to prepare PA1212 / PP-g-MAH blends. The effect of PP-g-MAH graft ratio and concentration on the mechanical properties and rheological behaviors had been investigated. Introduction of PP-g-MAH can improve the impact strength of PA1212 effectively, the rheological curves for blends with different graft ratios PP-g-MAH exhibit obvious “gel points”, and the blends corresponding to gel points show relatively higher impact strength than those of other blends. These results indicated the “gel points” acquired from the dynamic rheological data and the “super-toughness points”of the blends have a corresponding relationship and the super-toughness point could be conveniently determined by the dynamic rheological measurements.

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纤维性海藻酸钠水凝胶

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海藻酸钠(SA)是从褐藻中提取的一种由 β -D甘露糖醛酸盐和 α -L古罗糖醛酸盐连接的线性共聚物组成的天然聚电解质, 来源广泛, 具有高透氧性、止血性以及良好的生物降解性和相容性, 使得它在诸多领域都有广泛的应用。本文主要研究了SA在不同溶剂环境下的自组装行为, 并对自组装形成的凝胶的力学性能、响应性、注射性和回复性进行了探讨。研究结果表明, 含盐溶剂、含醇溶剂和高浓度都会诱导SA溶液发生纤维化再到凝胶化的转变。TEM和AFM测试表明凝胶内具有纳米纤维结构; SEM测试表明凝胶内部为疏松多孔结构。动态流变扫描的结果显示凝胶具有较高的强度, 可用作植入性水凝胶; 温度测试结果表明凝胶随温度的增加发生了凝胶-溶液的转变, 可用作温敏性材料; 挤出测试表明凝胶具有较好的注射性, 并且具有很好的回复性, 可以应用于3D打印。

关键词: 海藻酸钠; 纳米纤维; 水凝胶; 流变学

Fibrous sodium alginate hydrogel

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Abstract: Alginate is a natural polyelectrolyte extracted from brown algae species and made up of a linear copolymer of (1-4)-linked β -D-mannuronic acid (M) and α -L-guluronic acid (G) units. Sodium alginate is abundant, widely available, highly oxygen-permeable and hemostatic, as well as biodegradable and biocompatible, so that widely used in various fields. In the present work, the behavior of self-assembly of sodium alginate has researched in different solvent. The mechanical properties, responsive, injection and recovery of the gel formed by self-assembly were studied. The result shows that the fibrosis of the SA solution and the sol-gel transition induced by the salt solution, alcohol solvent and high concentration. The formation of nanofibril in the gel was determined by TEM and SEM, which also shows that the gel is porous. The results of dynamic rheological scanning display high strength of the gel that can be used as an implanted hydrogel. The transformation of gel-sol with increase of temperature, it can be used as temperature sensitive materials. Extrusion tests show that gel has excellent injection, and has a good recovery, what can be applied to 3D printing.

Key Words: Sodium alginate, Nanofibril, Hydrogel, Rheology

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聚丙烯的熔融支化改性及其结构演变

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利用过氧化物熔融引发的方法, 使聚丙烯在多官能度接枝单体和自由基调控剂的作用下发生熔融自由基文化反应。实验证明, 在严格控制反应条件的前提下, 改性的聚丙烯产物具有长链文化结构, 其熔体强度高, 抗熔垂性能优异。实验发现, 通过改变多官能度接枝单体和自由基调控剂的种类及剂量, 可以明显改变聚丙烯的分子链结构, 其中, 聚丙烯的长链文化结构对其熔体特性影响显著, 长支链的存在使聚丙烯的各项流变性能都有所改变。在此基础上, 此处以转矩-时间曲线为参照, 在不同反应时间点进行取样分析, 考察反应时间对改性PP产物熔体结构和熔体特性的影响, 并对聚丙烯熔融自由基文化反应的过程以及聚丙烯在熔融自由基文化反应过程中的结构演变进行详细探讨。

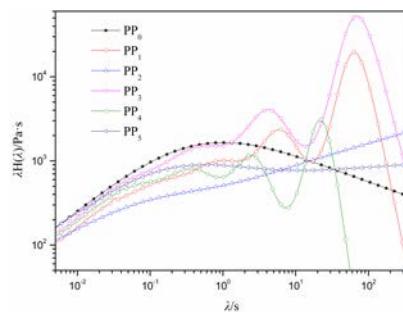


Fig. 1 Weighted relaxation spectrum for the virgin PP and modified PPs at 190 °C

关键词: 聚丙烯; 熔融; 长链文化; 熔体强度; 流变

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Melt Branching Modification of Polypropylene and its Architecture Evolution

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Melt radical branching reaction of polypropylene (PP) initiated by peroxide has taken place in the presence of polyfunctional monomer and radicals control agent. Long chain branching (LCB) structure was verified in the modified PP and LCB could change the melt properties of PP obviously. Category and dosage of polyfunctional monomer and radicals control agent could vary the chain structure of PP remarkably, which make great change in their rheological properties. Depending on the torque-time curve, some samples with different reaction times were chosen to analyze the reaction course and structure evolution of PP.

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聚电解质复合溶液的剪切诱导自增稠研究

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缔合型聚电解质因为包含大量缔合基团, 其结构通常较为复杂。自 Eliassaf 等发现聚甲基丙烯酸 poly(methacrylic acid) (PMA) 溶液会因分子缔合作用导致可自发回复的剪切增粘现象以来, 各种因疏水作用、氢键、金属络合作用导致剪切增粘的体系被陆续报道。近来, 接枝共聚型聚电解质——壳聚糖-丙烯酰胺共聚物 (CS-g-PAM) 的水溶液被发现会呈现一种独特的剪切诱导自增粘现象 (Shear induced self-thickening) ——在临界浓度以上, GPAM 溶液在强剪切下会首先呈现剪切变稀。停止剪切后, 体系黏度持续增加, 其最终黏度远高于初始溶液, 且其增粘效果不会自发回复。与传统的高分子剪切增粘相比, 该现象在增粘过程、增粘效果和增韧程度是否可控上都显著区别于之前报道的各种现象。本文通过研究 GPAM 与环糊精复合溶液的流变行为, 通过控制组成比和浓度等进一步实现了对复合溶液流变行为的调控。为认识和利用这种特殊流变行为在拓展聚电解质材料应用范围、提高聚电解质材料工程应用功效方面积累了必要经验。

关键词: 流变行为; 剪切诱导自增粘; 聚电解质; 氢键作用

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纳米二氧化钛/支化聚氧化乙烯高强非晶聚合物复合膜的制备

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聚氧化乙烯是一种可溶解无机盐类且具有一定离子传导性质的聚合物基体。目前, 聚氧化乙烯已被广泛应用于超级电容器、锂离子电池、燃料电池和染料敏化太阳能电池聚合物电解质等相关领域的研究[1-2]。然而, 聚氧化乙烯在作为电解质基体的使用过程中存在如下两个主要问题。首先, 聚氧化乙烯的高结晶度导致离子与聚氧化乙烯链段的相互作用较弱。通常, 聚氧化乙烯的分子量越高, 力学性能越好, 但是相应地, 聚合物越容易发生结晶, 离子传输性能变差。其二, 具有线性结构的聚氧化乙烯在电解液中存在溶解问题。溶解后的聚氧化乙烯的力学性能基本丧失。针对以上问题, 我们提出采用一种具有短链支化聚氧化乙烯且含活性碳碳双键的单体(P80), 并加入交联剂、光引发剂以及纳米二氧化钛, 在紫外光作用下制备了一种具有非晶支化聚合物结构且力学性能优异的新型聚合物复合膜, 如图1所示。该聚合物复合膜在电化学器件聚合物电解质中具有潜在的应用前景。

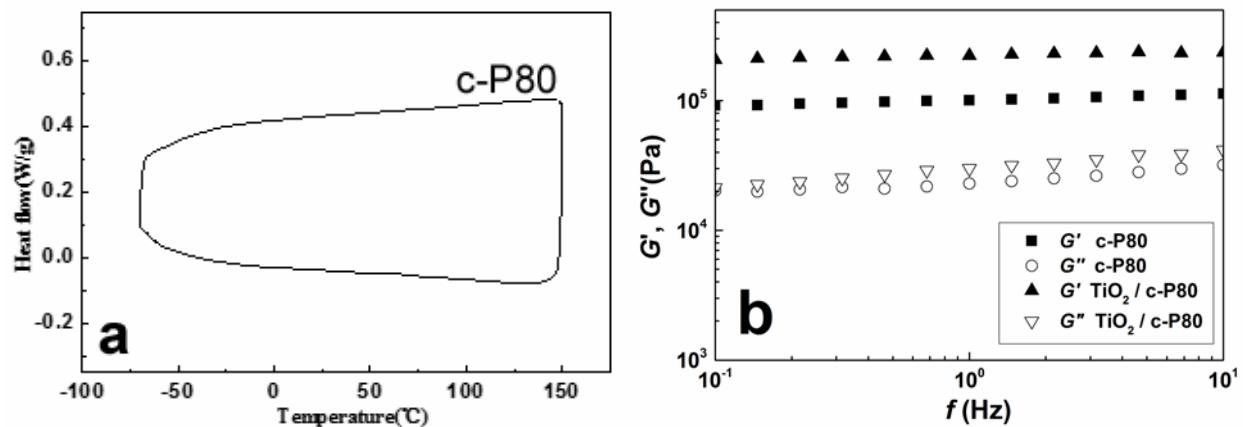


Fig. 1 (a) Differential scanning calorimetry curve of c-P80; (b) rheological properties of c-P80 samples with and without TiO_2

关键词: 支化聚氧化乙烯; 纳米二氧化钛; 高强聚合物膜; 非晶高分子

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Synthesization of Amorphous Polymer Membrane of Nano-Titanium Dioxide and Branched Polyoxyethylene with High Strength

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Nowadays, Polyethylene oxide (PEO) has been widely applied for polymer electrolyte in supercapacitors, lithium-ion batteries, fuel cells and dye-sensitized solar cell, and other related fields [1-2]. However, there are two main problems as follows. Firstly, the high crystallinity of PEO can result in the weak interaction between ions and PEO segments. Secondly, the PEO chain usually has a linear structure, so it can be dissolved in the presence of

liquid electrolyte. Mechanical properties of dissolved PEO chains are substantially lost. To solve these problems, we propose the use of a type of monomers (P80) which own short and branched PEO chains and also contain reactive carbon double bond, and a crosslinking agent, a photo-initiator, and nano titanium dioxide are added. Under UV irradiation, a branched and amorphous polymer structure containing PEO segments for preparing a novel polymer composite polymer film is obtained with excellent mechanical properties. It is believed that the polymer composite film has potential applications in the polymer electrolyte of electrochemical devices.

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一种有机硼交联剂的性能研究

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摘要: 目前, 油气开采中绝大多数井都需要进行压裂实现工业生产。现有交联压裂液技术主要是以瓜尔胶为代表的植物胶类天然多糖化合物, 通过硼酸盐等对骨架双羟基形成交联作用来调节水溶液的流变性能, 但由于成本较高, 在目前低油价下较难应用。本文报道了可降低交联压裂液成本的新型交联体系。通过表面胺基修饰的纳米二氧化硅与与硼酸酯合成得到的有机硼交联剂, 可降低聚合物浓度。利用XPS等波谱手段对冻胶结构进行分析。研究结果表明新型交联剂对瓜尔胶溶液的交联性能与相同摩尔浓度的硼酸钠相比, 还表现出更好的耐温耐剪切能力等流变性能。

关键词: 交联; 合成硼酸酯; 流变性能

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Performance Research of an Organic Borate Cross-linker

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Abstract: Nowadays, hydraulic fracturing is the most common method to increasing oil and gas production. The present fracturing fluid chemistry is mainly refers to guar gum, a typical natural polysaccharide plant gum, by cross-linking with borate salt at *cis*-dihydroxy site to control the rheology of the polymer solution. Due to the low crude oil price, it is expansive to application high concentration guar gum for fracturing. To reduce the polymer concentration and the cost of the stimulation as well, herein a novel cross-linker was syntheses from surface modified nano silica oxide with borate ester, and analyzed by XPS and SEM. The viscosity and rheology of the cross-linker reacted with guar solution was investigated. The results showed that, compared with the sodium borate, the synthetic cross-linker to give better thermo-stability and shear-resistance of the cross-linked guar solution.

Keywords Cross-link, Synthetic borate ester, Rheology performance

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气相白炭黑/聚醚复合体系的胺促凝胶行为

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研究了气相白炭黑/聚醚复合体系的流变行为, 发现微量有机胺可促进其凝胶化。胺促凝胶行为的促进依赖于气相白炭黑的表面化学性状, 可使亲水白炭黑体系凝胶点 ϕ_c 由 0.11 降至 0.02; 对于疏水型白炭黑体系, ϕ_c 仅由 0.16 降至 0.13。建立了“玻璃层逾渗”理论, 发现凝胶化的主要原因是包括粒子表面固定化的“玻璃层”在内的粒子相间发生几何学逾渗, 形成粒子相网络结构。揭示了胺促凝胶化机理。胺作为强质子受体, 提高了气相白炭黑粒子附近聚醚分子间的氢键网络密度, 造成非晶层中聚醚链段松弛能力进一步受限, 使非晶层转变为玻璃层(发玻璃层增厚), 增加了粒子相有效体积显著增大, 从而使复合体系在较低 ϕ 即发生玻璃层逾渗。

关键词: 气相白炭黑, 聚醚, 复合体系, 凝胶, 胺

Amine-promoted gelation of fumed silica/polyether system

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Amine induced gelation in fumed silica filled polyether has been investigated. It is found that introducing a trace amount of secondary/tertiary amine promotes gelation of hydrophilic silica dispersions even at extremely low contents of silica (< 2 vol %). By MDSC, BDS, and rheology investigations, strong evidence is found that (i) the amine-promoted gelation is due to thickening and easy-percolation of the inner glassy layer converted from an outer uncyclizable layer, and (ii) the dispersion rheology could be well normalized within the framework of a two-phase model incorporating effective volume fraction of nanoparticles plus the glassy layers. The thickening extent of glassy layer and rheology depends on both surface chemistry of FS and amine concentration.

Keywords: fumed silica, polyether, composites, gelation, amine

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白炭黑填充聚二甲基硅氧烷体系流变行为的研究

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采用共混法制备白炭黑(SiO_2)/聚二甲基硅氧烷(PDMS)复合材料, 考察了PDMS分子量($M_w=2\sim8 \text{ kg/mol}$)、填料含量及填料表面性质(亲水或疏水)对其流变行为的影响。动态应变扫描中, 疏水白炭黑(R974)/PDMS体系随应变增加依次出现软化-硬化-软化现象, 而亲水白炭黑(A200)/PDMS体系在线性区以外仅出现软化现象。分析临界软化点和硬化点, 发现临界硬化点和第二临界软化点分别出现在应变为50%、150%处, 与组成无关。相反, 第一临界应变软化点取决于诸多因素。采用可逆或非可逆网络模型可解释复合体系不同的流变行为。分析白炭黑的补强机理及剪切过程中的微观结构变化, 揭示了流体动力学补强对高频流变的关键作用及粒子间相互作用对低频流变的重要作用。

关键词: 气相二氧化硅; 聚二甲基硅氧烷; 分子量; 流变; 补强机理

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Rheology of fumed silica/polydimethylsiloxane suspensions

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In this study, rheological behaviors of fumed silica filled polydimethylsiloxane suspensions were investigated with varying molecular weight of PDMS ($M_w=2\sim8 \text{ kg/mol}$), silica concentration and surface characteristics (hydrophilic or hydrophobic). It is interesting that R974/PDMS suspensions exhibit softening-hardening-softening response with increasing dynamic strain at frequency 1 Hz while A200/PDMS suspensions show a sustained softening beyond the linear regime. Furthermore, the onset of softening and hardening can be normalized: the hardening is initiated by a critical strain of 50 % and the critical strain of the second softening is 150 %. On the other hand, the critical strain of the first softening depends on many aspects. We use the form of irreversible and reversible network model to explain the different nonlinear rheological behaviors of these suspensions. At last, the mechanisms involved in the generation of reinforcement and their structural evolutions during shear are thoroughly clarified. We can draw a conclusion that the hydrodynamic influence plays a critical role in the mechanism of reinforcement at high frequencies, while the interaction between particles matter most at low frequencies.

以聚醚胺基烷基糖苷为主剂的类油基钻井液研究

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针对油基钻井液环保压力大、配制成本高等瓶颈问题, 开展了环保型、低成本、高性能的聚醚胺基烷基糖苷(NAPG)类油基钻井液研究。以NAPG作为核心主剂, 优选增粘剂、降滤失剂、封堵剂等配伍处理剂, 通过钻井液体系构建及配方优化, 形成了环保型、低成本、高性能的NAPG类油基钻井液体系。对钻井液性能进行了评价, 结果表明: 钻井液页岩一次回收率为99.90%, 相对回收率为99.98%; 钻井液抗温达150°C, 流变性好, 动塑比0.327, 初终切适宜, 中压滤失量0mL、高温高压滤失量6.0mL; 润滑系数降低率达69.62%; 滤液表面张力26.60 mN/m; 钻井液抗盐达饱和, 抗钙10%, 抗土、钻屑20%, 抗水40%, 抗原油20%; 岩心动静态渗透率恢复值为91.4%和96.8%; 钻井液EC₅₀值为528800 mg/L, 无生物毒性。对NAPG类油基钻井液和油基钻井液从抑制、润滑、降滤失、储层保护及生物毒性等方面进行了对比, 结果表明, 两者性能相当, 且类油基钻井液在环保方面具有显著优势。NAPG类油基钻井液适用于强水敏性泥岩、含泥岩等易坍塌地层及页岩气水平井钻井施工, 可缓解目前油基钻井液环保压力, 扩大水基钻井液适用范围, 具有较好的推广应用前景。

关键词: 类油基; 钻井液; 聚醚胺基烷基糖苷; 页岩气; 强抑制

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Study on the similar oil based drilling fluid used polyether amine alkyl glucoside as the main treating agent

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In view of the problems of environmental protection pressure and high preparation cost for the oil based drilling fluid, the research of NAPG similar oil based drilling fluids with the advantages of green, low cost and high performance was carried out. Taking the NAPG produc as the main treating agent, the compatibility treatment agents including tackifier, filtration reducing agent and plugging agent were selected out, through the construction of drilling fluid system and formulation optimization, NAPG similar oil based drilling fluids with the advantages of green, low cost and high performance was formed. NAPG similar oil based drilling fluid is suitable for the high water sensitive mudstone, shale and other easy to collapse formation and shale gas horizontal well drilling construction, which can ease the current environmental protection pressure of oil based drilling fluid, expand the application scope of of water-based drilling fluid, and has a good prospect of popularization and application.

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外加盐对海藻酸钠溶液流变行为的影响

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海藻酸钠 (Sodium Alginate, SA) 是一种被广泛研究的聚阴离子电解质, 其功能性与加工性受到外加盐的显著影响。本文通过旋转流变仪研究了 SA 在水溶液和 0.2M NaCl 盐溶液中的稳态粘度的浓度依赖性, 依此标度关系得到两者的浓度分区图。在无盐情况下, SA 溶液划分为稀溶液、亚浓非缠结溶液、亚浓缠结溶液以及浓溶液四个浓度区域, 对应的标度关系分别为 $\eta_{sp} \sim C$ 、 $\eta_{sp} \sim C^{1/2}$ 、 $\eta_{sp} \sim C^{3/2}$ 和 $\eta_{sp} \sim C^{7/2}$; 三个临界浓度分别为分子链开始重叠的浓度 (C^* , 0.02 wt%)、分子链开始缠结的浓度 (C_e , 0.2 wt%)、聚电解质电荷完全被屏蔽时的浓度 (C_D , 0.8 wt%)。加入 0.2M NaCl 后, SA 溶液分为三个浓度区域, 对应标度关系为 $\eta_{sp} \sim C$ 、 $\eta_{sp} \sim C^{3/2}$ 、 $\eta_{sp} \sim C^{39/10}$, 两个临界浓度为 $C^*=0.04$ wt% 和 $C_e=0.4$ wt%。加入外加盐后, SA 分子链发生收缩, 流体力学体积较少, 导致增比粘度的浓度依赖性增强, 临界浓度出现了明显的后移。另外, 考虑到 SA 在工业应用中对应的多为缠结溶液, 本文还着重研究了外加盐对 SA 浓溶液 (2 wt%) 体系的影响。在一定的盐浓度范围内, SA 粘度随着盐浓度的升高而上升, 当盐溶液浓度继续到一定的临近值, SA 溶液发生分相, 粘度出现下降。工艺条件 (外加盐顺序) 对于海藻酸钠的稳态流变行为产生显著的影响。在同等盐浓度下, 先加盐的零切粘度显著高于加盐体系, 并且前者分相时需要的盐浓度低于后者。

关键词: 海藻酸钠; 外加盐; 水凝胶; 流变学

Influence of salt on rheological behaviors of sodium alginate solutions

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Abstract: Sodium alginate (SA) is a polyanion electrolyte that is widely researched, can be used for medical, textile and food, etc. By addition of salt can influence its functionality and process ability. The viscosity as a function of concentration for SA in both salt-free solution and in 0.2MNaCl is investigated via rotational rheometer. In salt-free solution, four concentration regimes of viscosity scaling and three associated critical concentrations were observed. Four concentration regimes follow the scaling relations of $\eta_{sp} \sim C$, $\eta_{sp} \sim C^{1/2}$, $\eta_{sp} \sim C^{3/2}$ and $\eta_{sp} \sim C^{7/2}$. Three associated critical concentrations was $C^*=0.02$ wt%, $C_e=0.2$ wt% and $C_D=0.8$ wt%. In salt solution, only three concentration regimes ($\eta_{sp} \sim C$, $\eta_{sp} \sim C^{3/2}$, $\eta_{sp} \sim C^{39/10}$) and two critical concentrations ($C^*=0.04$ wt%, $C_e=0.4$ wt%) were observed. In the presence of salt, the polymer chain structure collapses and occupies much less space resulting in higher values of the critical concentrations. An increase in both C^* and C_e is observed in the presence of NaCl. In the range of salt concentration, the addition of monovalent salt increases the zero shear rate viscosity of the entangled polyelectrolyte solutions. When the concentration reaches to a critical value, concentration begin to separate the phase the viscosity decreases. Process conditions (adding salt order) influence Rheological Behaviors of Sodium Alginate. Under the same salt concentration, the zero shear rate viscosity of the adding salt first is higher than adding salt later and the salt concentration of separating phase is lower..

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一种以弹性恢复试验为核心的聚合物弹性评价新方法研究

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驱油过程中, 聚合物溶液的粘弹性对提高驱油效率有很大影响, 因此, 评价其粘弹性对研究及筛选聚合物至关重要。目前的评价指标都不能真实反映聚合物在不断流经收缩/扩张的油气通道后的弹性特征, 即无法反映聚合物在地层中经不断剪切后弹性是否发生了改变。因此, 亟需建立一种新方法来评价聚合物在驱油过程中的弹性特征。本文选取梳型聚合物(KYPAM-2)、水解聚丙烯酰胺(MO-4000)和疏水缔合(HTPW)三种类型的常用聚合物作为研究对象, 测定了聚合物溶液经不同剪切速率剪切后弹性模量G'的保留率, 由此建立了一种简单、实用的以弹性恢复试验为核心的聚合物弹性评价新方法, 来反映聚合物在地层中经不断剪切后弹性的变化, 解决了只依靠G'的大小以及G'平台区的频宽无法比较MO-4000和HTPW弹性强弱的问题, 且此评价方法不受聚合物浓度的影响。试验结果表明, KYPAM-2的弹性最强, MO-4000的弹性次之, HTPW的弹性最弱。此外, 岩心驱替实验和微观可视化驱替实验都证明了该方法的可行性以及准确性。

关键词: 聚合物; 弹性; 弹性恢复; G'保留率

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Investigation of a New Method to Evaluate Elasticity of Polymers Based on Elasticity-Recovery Experiment

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Abstract: Three polymers were selected as the research objects. Elasticity retention rate of the polymer solutions after sheared at different shear rate was measured, and a simple elasticity evaluation method of polymers was established based on this elasticity-recovery experiment. This method can reflect the variation of elasticity of polymers after sheared in formation, and solved the problem that the elasticity of MO-4000 and HTPW can not be distinguished only by the G' and the platform of G'.

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仿生纤维结构水凝胶构筑及其平面-螺旋可控变形

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捕蝇草、豆荚等植物器官能够在一定的环境下发生三维变形, 这与其特殊的梯度纤维结构有关。利用凝胶等高分子软材料实现类似的可控变形具有重要的科学意义和应用价值。其关键在于如何构筑复杂梯度结构并控制材料内部的应力分布。我们模拟豆荚层状纤维素结构, 使用多步光刻技术合成了具有双层间隔条纹的复合结构水凝胶, 并研究其在外界刺激下发生可控扭转螺旋变形。通过调整凝胶尺寸和条纹角度, 我们能够控制凝胶形成卷曲、圆柱螺旋、扭转螺旋等三维形状。此外, 我们还利用不同响应性高分子构筑条纹结构, 使复合凝胶能够在外界刺激下发生三维形状转换。以上成果展示了水凝胶复杂结构与三维变形的精确控制, 也为其它软材料结构与变形设计提供了思路。

关键词: 光刻, 纤维状结构, 螺旋, 可控变形, 水凝胶

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Bioinspired fibrous structural hydrogels with programmed planar-to-helical shape transformations

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Self-shaping materials that can morph in a controlled manner as seen in nature have raised increasing attentions due to their promising applications in actuators, soft robotics, flexible electronics, biomedical devices, etc. Here, we use multiple-step photolithographic method to construct composite gels with layered fibrous structures, which show programmed shape deformation under specific stimulus. By tuning the cross angle of layered fibrils and the dimensions of gels, we can control the final 3D structures of patterned gels, ranging from rolls, cylindrical helix, to twisted helix. In addition, different kinds of polymers can be easily patterned to different regions, which facilitate shape transformation between different 3D shapes. These results demonstrate the deliberate controllability of complex microstructure and deformations of gels, which should also be suitable to other soft materials.

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