高性能聚乙烯产品设计

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摘要 聚烯烃是国民经济建设和日常生活必不可少的重要基础材料和战略物资。目前,我国聚烯烃行业严重依赖进口,高端聚烯烃产品占进口量的一半以上,行业发展严重受制于人。金属有机催化理论的迅猛发展极大地增强了对聚合物分子结构的调控能力,使人们有可能设计出更多性能优异的聚烯烃新产品。但是,如何实现聚烯烃新产品的工业生产,并使之转化成为商品,是制约聚烯烃产品高性能化的瓶颈,涉及化学工程和高分子科学的深度交叉。本文分别从催化剂结构设计、非均相催化剂结构解析、聚合反应工艺以及产品加工工艺的层面介绍了当前聚乙烯高性能化的重要进展;重点介绍了从活性中心聚合微环境设计出发,通过与催化剂聚合行为的匹配,开发的高性能聚乙烯产品制备新工艺。利用烃类冷凝液的喷射蒸发,在单一流化床反应器中构建温度、浓度差异化的持液颗粒聚合和气相聚合共存的复合流型,打破流化床固有的温度浓度均一性特点,相继开发了超低/极低密度聚乙烯高端产品数万吨,率先生产热收缩膜、拉伸套管膜、双向拉伸聚乙烯膜等高端产品;利用催化剂在惰性组分纳微气泡富集区域的穿梭和碰撞,在生长的聚乙烯颗粒周围营造反应组分的传质开关,使分子链生长和结晶有节奏地交替进行,降低了初生态聚乙烯的链缠结程度,开发了易加工的超高分子量聚乙烯产品。

关键词 高端聚乙烯, 非均相催化, 聚合工艺, 多级结构

高分子材料是国民经济建设和日常生活必不可少的重要材料,而聚烯烃塑料是其中的重要组成部分。2020年,我国聚烯烃材料产能已经突破4000万吨,“十四五”期间聚烯烃规划产能更是将突破7000万吨。如此巨大的产能下,我国聚烯烃行业仍然严重依赖进口,高端产品的进口量占50%以上。在航空航天、电力、新能源汽车等行业,产品进口率接近100%。2025年,我国高端聚烯烃需求量将达到1115万吨,自给率仅为69%,行业呈现低端产品过剩、中高端产品不足、高端产品严重依赖进口、核心技术长期受制于国外的卡脖子现象^[1]。

聚烯烃具有十分复杂的多级结构,包括分子链结构和聚集态结构。其中,分子链结构有组分组成、分子量及其分布、支链序列结构、等规度等;聚集态结构主要包括分子链的链缠结、结晶和取向等^[2,3]。丰富的多级结构赋予了材料诸多优异性能。然而,也正是由于聚烯烃复杂的多级结构,使得高端聚烯烃产品开发充满挑战。因此,如何调控多级结构的定向排列,赋予聚烯烃如刚性、韧性、强度,以及极性、热学、电学和光学等诸多性能,是实现聚烯烃产品高端化、差异化、多元化的必由之路。本文分别从催化剂工程、反应工艺与工程以及产品加工工程的角度阐述聚烯烃高

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性能化领域的进展和局限,期望通过学科之间的交叉融合,为高性能聚烯烃的工业生产和新牌号开发提供新思路。

1 催化剂工程与聚烯烃高性能化

1.1 均相催化剂

20世纪50年代, Ziegler-Natta催化剂的发明将聚烯烃合成由高温高压(300°C、300 MPa)的苛刻聚合条件带入温和的低温低压反应环境。研究人员在聚烯烃分子链结构设计方面不断取得新突破,先后出现了茂金属催化剂、后过渡金属催化剂等具有跨时代意义的催化体系。近年来,化学工作者基于金属有机催化理论,从配体结构设计、金属中心特性等方面实现了聚烯烃分子链结构的准确、高效设计,可以制备支化、接枝、嵌段、交联结构以及极性聚烯烃等聚烯烃材料^[4-7]。分子链结构的改变能够实现产品亲和性、结晶性、力学性能和流变学行为的可控调节,进而赋予了聚烯烃更加丰富的功能性^[8]。

前过渡金属催化剂(Ti、Zr、Hf)对乙烯、丙烯以及 α -烯烃聚合表现出优异的催化性能,通过配体结构修饰在分子量上能够实现从小分子齐聚到超高分子量聚乙烯的高效制备,涌现出诸多优异的催化剂^[9-17](图1)。在支化结构上,能够实现线性聚烯烃和聚烯烃弹性体(如限制几何构型催化剂)的超高活性生产;在分子量分

布上,能够精准地进行活性聚合,实现聚乙烯分子量、分子量分布的可控设计。然而,由于金属活性中心对极性原子具有较强的亲和性,在进行极性单体共聚时,极性单体中双键与极性基团之间需有阻隔链,增大极性基团与金属中心的距离,进而保护活性中心。

1995年, Brookhart课题组^[18]发明的含大位阻取代基团的 α -二亚胺钼系、镍系催化剂,以高活性制备了从线性到超支化、再到极性单体共聚的一系列聚乙烯,解决了之前过渡金属催化剂只能催化乙烯寡聚的问题。与前过渡金属催化剂不同,后过渡金属催化剂在制备支化聚烯烃时,可通过“链行走”机理,以乙烯为唯一单体制备支化甚至超支化聚烯烃(图2(a))^[19-21]。与前过渡金属相比, Ni、Pd等后过渡金属具有更低的亲氧性,对O、S、N等杂原子具有容忍性,不易被毒化,因而具有良好的稳定性。Mecking课题组^[22,23]通过配体修饰的后过渡金属催化剂首次实现了聚烯烃的水相聚合;并基于乳液聚合的思想,将生长的分子链利用乳化效应彼此分开,进而获得了理想的聚乙烯纳米晶体,结晶度可达97%(图2(b))。然而,后过渡金属催化剂在进行极性单体共聚时催化剂活性不够高、分子量大幅下降,产品应用价值欠佳;催化剂热稳定性差,在60°C以上的聚合反应中很快失活。对于强放热的乙烯聚合过程,如此低的聚合温度无法满足工业生产时反应热撤热的要求,限制了这类催化剂的工业应用。Guan课题组^[24,25]报道了含环番基团的 α -二亚胺镍催化剂,催化剂的热稳定

图1 典型的前过渡催化剂体系^[9-17]

Figure 1 Typical transition metal catalyst system^[9-17]

性和聚合物的分子量与经典的 α -二亚胺镍催化剂相比都有显著提升(图2(c)). Brookhart课题组^[26]报道了一种具有“三明治”结构的 α -二亚胺镍催化剂, 8-对甲苯基团提供了更稳定的轴向位阻, 降低了链转移反应, 提高聚合物分子量的同时, 降低了分子量分布. 分子量达百万级的超高分子量聚乙烯的分子量分布仅为1.8, 聚合物的支化度可提升至152/1000C. 然而, 大位阻的配体使得乙烯配位困难, 聚合活性下降了1~2个数量级(图2(d)). Chen课题组^[27~31]从催化剂的结构设计入手, 通过调控电子效应、位阻渐变效应等策略, 发展了一系列后过渡金属镍钯催化剂, 并能够实现极性单体共聚物分子链结构的灵活调控, 聚合物支化度为25/1000C~116/1000C, 分子量为 $0.2 \times 10^4 \sim 164 \times 10^4$ g/mol(图2(e)). 目前, 后过渡金属催化剂已经实现了共聚物微观结构从高度支化(>100/1000C)到高度线性(<1/1000C)的灵活设计, 并突破了前过渡金属催化剂需用极性基团阻隔剂的限制, 实现了极性单体的普适性^[32~34](图2).

1.2 非均相催化剂

需要指出的是, 工业装置上使用的聚烯烃催化剂90%为负载型催化剂. 这就意味着大多数均相催化剂应用于工业装置时, 必须解决催化剂负载化的问题, 进而实现对聚合反应动力学、产品颗粒形貌等重要工程参数的理性调控, 以满足工业稳定生产的需求.

活性中心的多样性是负载型非均相催化剂在产品结构调控中面临的普遍性问题, 也是其与均相催化剂的本质区别. 多样性的首要来源是载体物化环境的不均一性(图3). 以经典的 MgCl_2 载体为例, 其多种晶面上分布着具有不同配位数的 Mg^{2+} 位点, 并且相同配位数但配位环境不同的 Mg^{2+} 也具有不同的化学环境, 制备的聚合物往往也具有不同的分子量以及不同的乙烯和 α -烯烃共聚能力^[35~37]. 除此之外, 负载型Ziegler-Natta催化剂多组分相互作用的特点也是导致活性中心多样性的重要原因. Comito等人^[38]采用离子交换技术将 VCl_3 负载在金属有机框架材料(metal-organic framework, MOF)的金属节点上. MOF框架的骨架结构实现了V活

图2 典型的后过渡金属催化体系^[18~34]. (a) 含大位阻取代基团的 α -二亚胺钯系、镍系催化剂; (b) 水溶性镍系催化剂; (c) 含环番基团的镍催化剂; (d) 具有“三明治”结构的(8-对甲苯基 α -二亚胺)镍催化剂; (e) α -二亚胺镍催化剂; (f) α -二亚胺钯催化剂

Figure 2 Typical late-transition metal catalyst system^[18~34]. (a) α -Diimine Pd(II) and Ni(II) catalysts containing large steric substitution groups; (b) water-soluble Ni(II) catalyst; (c) cyclophane-based nickel catalyst; (d) “sandwich” (8-*p*-tolyl naphthyl α -diimine)nickel(II) catalysts; (e) α -diimine nickel catalyst; (f) α -diimine Pd(II) complex

性中心的单分子负载, 聚乙烯产物分子量分布可缩小至3.0. Diesing等人^[39]采用交联聚苯乙烯(crosslinked polystyrene, CL-PS)微球负载茂金属催化剂. CL-PS在甲苯中溶胀, 形成了众多由溶剂小分子填充的空穴. 这些空穴为聚乙烯的链增长提供了弹性空间, 构建了拟均相的聚合微环境, 可窄化聚合产物的分子量分布. 空穴周围的CL-PS分子链能够控制乙烯传质速率, 使催化剂活性平稳释放.

目前, 非均相催化剂的工作大多集中于通过活性中心负载微环境设计, 调控聚烯烃分子结构, 极少涉及聚集态结构的调控, 在一定程度上限制了聚烯烃高性能化的发展. Rastogi课题组^[40-42]将FI催化剂负载于纳米无机颗粒表面(单壁纳米碳管和 TiO_2). 纳米颗粒上有限的负载位能够降低链交叠的发生概率; 同时, 25°C 的聚合温度保证了初生链段的快速结晶, 有利于降低初

生态聚乙烯的链缠结程度^[43]. 该过程避免了反应器黏壁现象, 节省了助催化剂用量. 低缠结的超高分子量聚乙烯(ultra-high molecular weight polyethylene, UHMWPE)能在低于熔点温度下($125\sim 145^\circ\text{C}$)进行单轴超倍拉伸(188倍)^[44,45]. 然而, 为保证纳米颗粒在聚合溶剂中良好的分散, 纳米颗粒需经过复杂的改性过程, 大大增加了催化剂的制备成本和难度. 此外, 受制于纳米颗粒几何结构、分散性和有限的负载位等因素, 催化剂大多负载于纳米粒子团聚体的表面, 且负载量低, 致使催化剂的活性低、产物灰分高(载体残留量达3%~10%, 重量百分比). 本课题组^[46-49]利用聚倍半硅氧烷与 MgCl_2 分子的配位作用, 在载体表面原位形成了尺寸为数十纳米的惰性微球, 实现了活性中心的有效分隔, 首次在工业聚合反应温度下($\geq 60^\circ\text{C}$)以极高的活性制备了低缠结UHMWPE(图4). 产品具有优异的烧结成型能

图3 非均相催化剂活性中心的多样性^[35-37]

Figure 3 The heterogeneity of active species in the heterogeneous catalyst^[35-37]

图4 非均相催化剂结构设计与初生态聚乙烯链缠结调控

Figure 4 The design of heterogeneous catalyst and its regulation on the entangled state of the nascent polymer

力,冲击性能得到大幅提升(+20%).

与均相催化剂相比,非均相催化剂的结构解析十分复杂,如何解析负载型催化剂活性中心的微观结构(活性中心组成、结构、分布等),揭示催化剂负载机理、聚合机理及链段结构演变规律,是设计非均相催化剂的关键.传统的核磁共振谱、升温淋洗分级等手段通过分析聚合物的微观结构倒推活性中心可能的特征(图5)是一种间接的分析活性中心结构信息的方法^[50-52].但是,这种间接的倒推式方法无法实现分子链级别的解耦,因此也无法给出准确的活性中心结构特点.构建模型催化剂、揭示催化剂聚合过程中活性中心的演变特点,是一种直接了解活性中心结构特征的手段. Somorjai课题组^[53-57]以Pd为基底外延生长MgCl₂薄膜,并将该薄膜作为模型载体负载TiCl₄.该催化剂克服了催化剂表面电荷富集的问题,能够采用X射线光电子能谱、离子散射谱和程序升温脱附等方法来研究催化剂在制备过程中表面活性物种的变化情况.有研究在此基础上将电子顺磁共振技术应用于类似的模型催化剂^[58-60],分析了表面钛离子在烷基铝活化和乙烯聚合初始阶段的价态变化.研究表明,氯原子在MgCl₂表面具有很高的机动性,能够快速迁移至表面缺陷处的不饱和配位Mg²⁺,这种动态特性对于决定TiCl₄与不同给电子体之间的相互作用至关重要.

红外光谱和拉曼光谱等振动光谱对物质的原子类型、化学键、几何构型等特点极其敏感,对极低浓度的物质也有很好的响应,可以在较低的活性中心负载浓度下解析活性中心的多样性,是近年来逐步发展起来的活性中心结构解析手段. Brambilla等人^[61]同时采

用漫反射红外光谱和拉曼光谱,以MgCl₂/TiCl₄二元催化体系和MgCl₂/TiCl₄/ID三元体系为对象,系统研究了给电子体的作用机理.以邻苯二甲酸二丁酯(DBP)体系为例,其主要特征吸收峰为苯环C=O伸缩振动区间1650~1700 cm⁻¹和邻苯二甲酰氯化物C=O伸缩振动峰1750 cm⁻¹.当三乙基铝(TEA)活化后,1750 cm⁻¹处邻苯二甲酰氯化物峰强度大幅下降,表明该物质基本被TEA除去.与此同时,1700 cm⁻¹处吸收峰位置发生红移,表明有不同结构的DBP-M复合物生成,这与拉曼光谱观察到的实验结果一致.近些年, Groppo课题组^[62,63]采用直接钛化法,以代表MgCl₂/TiCl₄/乙醇体系的表面模型催化剂为研究对象,成功跟踪了从载体活化到TiCl₄负载、烷基铝活化以及最终的乙烯聚合等过程中催化剂的红外信号变化,并得到了表面物种的重要组成和结构信息.研究表明, MgCl₂/乙醇载体在升温脱醇过程会经历几个过渡态的转换,以此来获得热活化后载体的高比表面积,同时伴随着一些醇类副产物的产生.对负载过程的在线分析结果表明, TiCl₄在MgCl₂上的吸附主要分为两个步骤: (1) 以物理吸附的形式分散在MgCl₂表面; (2) 通过强配位作用化学吸附在不饱和配位Mg²⁺位点上.三乙基铝的加入会导致部分表面TiCl_x物质聚集形成Ti团簇.本课题组^[64,65]利用原位红外光谱技术首次发现了MgCl₂/THF/TiCl₄催化剂中THF的高机动性(图6).该动态属性对于活性中心的形成和分布起着关键性的作用.在TiCl₄负载过程中, THF的高机动性使其可以从MgCl₂表面部分脱附,使得载体中原本被THF覆盖的6配位Mg²⁺重新变为不饱和状态,因而形成了可供TiCl₄插入的空位.待TiCl₄通过

图5 聚合物结构倒推活性中心结构分析方法^[50-52]

Figure 5 Reverse deduction method for the analysis of active species^[50-52]

图6 原位红外光谱技术在活性中心结构解析的应用

Figure 6 Characterization of active species using *in-situ* Fourier transform infrared spectrometer method

Ti-Cl-Mg键配位在生成的不饱和 Mg^{2+} 上, THF分子的动态特性使其从 MgCl_2 迁移至表面吸附的 TiCl_4 分子上, 从而形成 TiCl_4 -THF配合物; 经过进一步的分子结构重排后, 形成了具有6配位八面体稳定结构的 $(\text{THF})_2$ - TiCl_4 -Mg活性中心。

近年来, 随着X射线近边吸收谱、X射线叠层成像谱等高精细分辨谱线在非均相催化剂上的表征, 活性中心周围的配位环境、空间分布等特征也逐渐得到解析。这为人们准确理解非均相催化剂活性中心结构特征, 理性设计催化剂结构, 进而实现聚烯烃微观结构的可控设计奠定了基础。

2 聚合反应工程与聚烯烃高性能化

在众多聚乙烯的生产工艺中, 流化床乙烯聚合工艺占到40%的产能, 属于主流工艺^[66]。该工艺流程短, 操作简便, 能够生产全密度的聚乙烯产品^[67]。但也正是由于其流程短, 使得其调节手段少, 流化床工艺的产品

结构单一、工艺竞争力弱, 生产的产品中通用料占到95%以上, 专用料缺口非常突出(图7(a))^[68]。此外, 为获得高的单体浓度, 流化床反应器通常在露点附近进行操作, 进而获得更高的催化活性。由于流化床反应器较差的传热能力, 颗粒温度过高往往引发结块的发生, 影响装置的稳定运行^[69-71]。北欧化工公司推出的环管-流化床聚乙烯工艺(图7(b)), 依次在环管反应器中生产低分子量线性聚乙烯, 在流化床反应器中生产高分子量高支化聚乙烯, 实现多种聚乙烯在单颗粒内的共混^[72]。采用该工艺生产的双峰聚乙烯具有优异的耐环境应力开裂, 能够生产PE100和PE100RC等高端聚乙烯管材料。然而, 由环管反应器的超临界状态闪蒸至低温低压状态时, 颗粒吸附的挥发分体积骤增导致的颗粒破裂, 使得环管-流化床串联工艺存在大量的细粉, 影响了装置稳定运行。

淤浆聚合工艺是广泛使用的聚乙烯生产工艺, 能够生产熔融指数为(0.01~150) g/10 min, 密度为

图7 经典的聚合反应工艺流程示意图. (a) 气相流化床工艺; (b) 环管-流化床组合工艺

Figure 7 Typical polymerization process for the synthesis of polyethylene. (a) Gas phase fluidized bed process; (b) loop fluidized bed combined process

0.918~0.98 kg/m³的树脂. 淤浆聚合需要采用丙烷、异丁烷、己烷和庚烷等惰性的稀释剂, 实现颗粒在溶剂中的悬浮, 稀释剂的使用提高了反应釜内传热能力. 与气相法相比, 淤浆工艺可在更高的聚合活性下操作. 多釜串联的淤浆工艺能够更加灵活地调控聚乙烯的分子链结构, 是高性能聚乙烯产品主流的生产工艺. 但是, 由于稀释剂对聚乙烯颗粒的溶胀效应, 淤浆工艺无法生产更低密度聚乙烯产品, 主要用于生产高密度聚乙烯. 巴塞尔聚烯烃公司的赫斯特低压淤浆工艺采用3个反应釜工艺^[73,74], 其工艺灵活, 反应釜可串联也可并联, 既能够生产单峰注塑或拉丝料, 也能够生产双峰管道料. 三釜串联工艺对聚乙烯产品分子量及其分布、支链序列结构的调控能力强, 能够兼顾产品的流动性、机械强度和抗环境应力开裂、抗蠕变和耐龟裂等性能, 是高性能聚烯烃产品生产的代表性工艺. 但是, 该工艺流程长, 需采用具有超长聚合活性的多活性中心Ziegler-Natta催化剂; 活性中心的多元性不可避免地产生低聚物, 容易黏结, 影响连续稳定生产. INEOS公司的IN-NOVENE S双环管工艺使用Ziegler-Natta催化剂与Cr系催化剂生产单峰和双峰高密度聚乙烯产品^[75], 该工艺采用低沸点的异丁烷为溶剂, 容易通过闪蒸除去. 环管工艺具有更加优异的撤热能力, 乙烯单程转化率高, 单耗和能耗较低, 单套产能大, 可达到45万吨/a.

本课题组^[76-78]从聚合反应器及工艺、催化剂的创新, 以及二者的协同匹配出发来设计定制聚烯烃的多级结构, 在单一气相流化床反应器内实现了聚乙烯的高性能化. 首先, 对聚合反应器的微环境(包括流场、温度场、浓度场和共聚单体种类)进行时间调变、空间调变或者时间空间同时调变. 在反应釜中连续增大

冷凝液量, 发现了介于气相聚合与淤浆聚合之间的持液颗粒聚合新模式, 显著提高了乙烯聚合活性及产品性能, 如产物支化度、片晶厚度等^[79,80], 持液颗粒聚合对聚合活性及产品性能具有显著的调控作用. 受此启发, 我们对流化床反应器中微环境进行空间调变. 通过烃类冷凝液的喷射蒸发, 在单一反应器中构建温度、浓度差异化的持液颗粒聚合(云区)和气相聚合(非云区)共存的复合流型, 打破流化床固有的温度浓度均一性特点^[81-88]. 随后, 将共聚/氢调行为差异明显的活性组分负载于载体颗粒内, 催化剂活性颗粒在不同区域的反复穿梭聚合, 生成链结构差异化明显的宽分布、高支化聚乙烯; 相继开发了超低/极低密度聚乙烯高端产品数万吨, 率先生产了热收缩膜、拉伸套管膜、双向拉伸聚乙烯膜等高端产品(图8(a)).

UHMWPE初生颗粒的链缠结极大地增加了产品熔体黏度, 无法采用传统的螺杆挤出方式进行产品加工, 因此加工效率极低^[89-91]. 过高的链缠结程度也限制了分子链取向能力, 力学性能无法达到预期. 工业反应温度下, 链增长速率远大于链结晶速率, 致使分子链来不及形成结晶而容易产生链缠结. 本课题组^[92,93]从活性链缠结形成机制出发, 开发了具备活性链解缠结功能的催化剂和聚合工艺. 在催化剂方面, 将惰性纳米微球植入催化剂表面, 增大活性链间距离, 实现活性链的解缠结; 在聚合工艺方面, 将直径为数十至数百微米的氮气微气泡引入淤浆聚合体系中, 微气泡与颗粒间平均接触时间(微气泡从接触颗粒至离开该颗粒的时间)的数量级为10⁻³ s, 该接触时间与聚合过程中链段的生长时间相匹配(~10⁻³ s). 另外, 微气泡与颗粒间的间歇时间(颗粒从与上一个微气泡分离到与下一个微气泡

图8 基于聚合工艺的聚乙烯产品高性能化。(a) 气液法聚合工艺; (b) 气泡辅助聚合工艺

Figure 8 The innovation of polymerization process for the synthesis of high-performance of polyethylene. (a) Gas-liquid polymerization process; (b) bubble-assisted polymerization process

接触的时间)的数量级也为 10^{-3} 。这说明微气泡与颗粒间频繁的接触/分离使得反应物向颗粒内的传质过程被间歇阻隔/恢复,产生“休眠效应”,在活性点周围周期性地断绝乙烯的供应,使活性链增长和结晶有节奏地进行,为初生的链段提供更加充足的结晶时间,实现了活性链的解缠结。由此,开发了低缠结、易加工的UHMWPE新产品(图8(b))。

3 聚乙烯的功能化改性技术

通用聚乙烯树脂虽然表现出良好的综合性能,但是仍然难以满足特定需求场景下的使用需求。因此,在加工过程中,往往需要进行功能化改性,以满足使用需求。这种改性方法主要从聚集态结构演变规律的调控出发,通过调节结晶取向、链缠结结构等聚集态结构特征,实现聚乙烯的高性能化^[94]。常用的功能化改性材料主要有纳米粒子、工程塑料、弹性体等材料。比如,刚性的碳酸钙、滑石粉等往往用于增强聚烯烃树脂,

韧性的聚烯烃弹性体可用于改善材料的耐冲击性能,超高分子量聚乙烯可用于改善聚烯烃的耐磨和润滑性能,玻纤材料与聚丙烯的掺混可提升产品的拉伸性能^[95~104]。聚乙烯功能化改性的关键是解决多组分之间的相容性。然而,掺杂的功能化粒子微观结构与聚烯烃材料区别很大,极易出现相分离,刚韧之间此消彼长的矛盾始终是高分子材料领域面临的重大挑战。

自增强复合材料(self-reinforced composites, SRCs)是指聚合物基体被相同聚合物组分的取向纤维、条带或颗粒改性增强后的材料^[105~108]。SRCs各组分微观结构相近,最大程度地保证了各组分之间的相容性,并使这类材料更易回收。自增强加工技术利用聚合组分的分子量分布,使特定链长的分子链在加工流场的特定位置形成取向,进而实现对聚合基体的增强(图9)。Capiati和Porter^[109]利用薄膜堆积加工工艺将高熔点的聚乙烯长丝与粉末混合,制备了聚烯烃共混物。加工时,聚合物基体即使熔融,取向的聚乙烯长丝仍未

图9 自增强聚乙烯产品制备与加工^[105,106]

Figure 9 Self-reinforced composites synthesized by the melting blending^[105,106]

被破坏,起到熔体支撑的作用,可将加工窗口提高10°C. Deng和Shalaby^[110]发现将UHMWPE纤维加入UHMWPE基体材料后,拉伸强度、拉伸模量和抗蠕变性能均有明显提升. Guan等人^[111]采用振动辅助注塑成型(vibration-assisted injection molding, VIM)加工手段,强化了高密度聚乙烯和UHMWPE共混物中shish-kebab串晶结构的形成. 共混物的杨氏模量可以从1.0提高至3.5 GPa,屈服强度可从23提高至87 MPa. Huang^[112]利用流动诱导结晶实现HDPE基体的自增强. HDPE熔体在接近收敛通道出口处,拉伸应变速率会急剧增大,HDPE分子链可以更好地发生取向结晶,进而增强了HDPE基体材料. 当模具压力低于40 MPa, HDPE自增强复合材料的拉伸强度能够提升8倍. Zhang等人^[113]采用振荡填料注塑成型工艺制备了HDPE/LDPE自增强复合物,复合物的韧性、拉伸强度和拉伸模量均大幅提升. Lei等人^[114,115]采用动态填充注塑成型工艺与外加单轴振荡应力场制备了PE和PP共混物. 结果表明,双轴增强的复合物能够形成大量的互锁shish-kebab串晶结构、取向分子链和片晶结构,结晶度提升,样条的拉伸强度在流动方向和横向方向均有42%的提升. 但是,在流动方向和横向的应力-应变行为与冲击强度却存在明显差异,这是因为两个流动方向上聚合物链段呈现非对称的微观结构. 有研究采用振荡剪切注塑成型工艺(oscillatory shear injection molding, OSIM)实现了对商业UHMWPE树脂的加工(图9)^[116~118]. 在加工过程中,首先将2%(重量百分比)商业UHMWPE与98%(重量百分比)低分子量聚乙烯LMWPE进行溶液共混以达

到分子链级别的混合,再将这种共混物加入UHMWPE基体,形成UHMWPE含量为40%(重量百分比)的UHMWPE/LMWPE复合物,最后经过OSIM注塑加工成为制品. OSIM加工工艺的特点在于在样品注塑冷却结晶过程中,持续施加剪切振动场作用,可抑制分子链的蠕动、松弛和缠结,并加强分子链的取向结晶行为,产品拉伸性能从27.6 MPa提高到78.4 MPa.

4 总结与展望

迄今为止,人们通过催化剂工程、化学反应工程和加工成型技术3个层面能够分别指导聚烯烃牌号的生产. 但是,由于各个层面控制着聚烯烃生成的不同要素,如链生长、晶型形成、颗粒形貌等,使得各个层面在分子结构和超结构上的调控能力无法兼顾. 一方面,存在天花板效应;另一方面,导致各层面的功能不协调、不匹配,无法发挥技术综合的最优效果,甚至引发安全问题. 因此,我们认为,加快聚烯烃高性能化的发展应当从聚合反应机理和分子链生长行为出发,匹配协同催化剂工程、化学反应工程和加工成型技术,并解决与催化剂特性相匹配的聚合工艺及反应器技术,催化剂、聚合工艺及反应器对聚烯烃多层次结构的协同调控,及聚烯烃多层次结构与性能的相互关系这三大科学问题,实现催化剂、聚合工艺及反应器的集成创新,聚合产物链与聚集态的协同优化,成套生产技术与产品的同步开发,获得具有我国自主知识产权的高性能聚乙烯成套技术,并实现聚乙烯工程技术的引领.

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Summary for “高性能聚乙烯产品设计”

Synthesis of high-performance polyethylene

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Polyolefin is one of the important and fundamental materials in daily life and has a great influence on the national economy. With the advances in catalysis in organometallic chemistry, the molecular structure of the polyolefins can be modulated reasonably, resulting in the design of high-performance polyolefins. However, synthesizing high-performance polyethylene on the industrial scale and making them a commodity is still a big challenge, thus limiting its current applications in chemical engineering, polymer engineering, and science. In this study, progress in the high-performance polyolefin synthesis is reviewed based on the design of homogeneous catalyst, heterogeneous catalyst, polymer reaction engineering, and product processing engineering. The *in situ* characterization of the evolution of active species is described based on advanced techniques favorable for revealing the catalytic behavior and synthesizing the polyolefin with the desired structure. In view of chemical engineering, the gas-liquid-fluidized bed process and bubble-assisted slurry polymerization process designed by our group are introduced for the synthesis of novel polyethylene commodities based on the matched behavior of catalytic performance and polymerization engineering. For example, using the jet evaporation of hydrocarbon condensate, a composite flow pattern of liquid-holding-particle polymerization and gas-phase polymerization with different temperatures and concentrations is constructed in a single fluidized bed reactor, breaking the inherent temperature and concentration uniformity of the fluidized bed. The catalyst can shuttle back and forth in this heterogeneous environment, where numerous polymer chains with diverse microstructures can be synthesized along with the chain propagation. This method ensures the most homogeneous distribution of different components since these components are mixed as soon as the chain grows. Thousands of tons of ultralow-/very-low-density polyethylene products have been developed successfully, which can produce high-performance products, such as heat-shrinkable film, stretch-casing film, and bidirectional stretch polyethylene film. Furthermore, ultrahigh molecular weight polyethylene (UHMWPE) has emerged as a value-added engineering polymer rather than a commodity plastic owing to its unprecedented properties. The ultrahigh molecular weights (i.e., larger than one million g/mol) with numerous entanglements serve as the physically crosslinked points, dramatically increasing the melt viscosity. This limits their processability and the resulting mechanical properties. We have proposed an inert nano- and microbubble-assisted polymerization process based on the reconstruction of the microchemical reaction environment around the active sites. The mean contact/interval time between microbubbles and particles is observed to be 10^{-3} s of the mean contact/interval time, several orders less than the chain propagation time. This frequent contact/separation model between microbubbles and polymer particles instantly blocks/recovers the reactant transfer on the solvent-particle interphase, causing an intermittent “dormancy effect” to retard chain propagation and facilitate chain crystallization. The processes of chain growth and chain crystallization are performed alternately, reducing the chain entanglement degree of nascent polyethylene. The nascent UHMWPE with reduced entanglements is achieved by the catalyst synthesizing the highly entangled polyethylene. The synchronous increment is found in stiffness, toughness, and strength for the synthesized polyethylene owing to reduced chain entanglements.

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