

·研究简报·

一种含树枝单元的高流动性尼龙 6 的原位聚合及性能测试^{*}

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摘 要 将低代数的树枝状大分子聚酰胺胺(polyamidoamine, 即 PAMAM)分别与对苯二甲酸配制成母盐溶液,再以母盐溶液、己内酰胺、封端剂一起投入高压釜进行原位聚合,通过调节 PAMAM 在己内酰胺中的比例及改变不同的 PAMAM 代数得到新型高流动性尼龙 6. FTIR 显示,与线性尼龙相比较,高流动性尼龙 6 的 $\gamma(\text{N-H})$ 和 $2\delta(\text{N-H})$ 两处对应峰都发生了明显的蓝移. 对于树枝单元含量较低 (0.3 wt% ~ 0.5 wt%) 的新型尼龙 6,拉伸性能没有下降,缺口冲击强度增加,而熔体流动却显著得到改善. DSC 显示,新型尼龙 6 的结晶曲线的结晶峰温度有不同程度的降低,晶体生长速率明显减慢.

关键词 尼龙 6, 高流动性, 聚酰胺胺, 原位聚合

聚酰胺胺(PAMAM)是一种树枝状结构聚合物,外围含有大量的活性官能团,近年来,在催化^[1],药物或基因载体^[2~4],螯合剂^[5],自组装^[6,7]等方面的应用和研究引起人们广泛关注,但在塑料工程领域的应用并不多见^[8].

提高尼龙的流动性,改善尼龙的加工性能是许多国际大公司竞相研究的热点. 大量文献显示^[9~13],往尼龙中加入少量的有机、无机分子或低聚体,通过共混的方式,均能得到高流动性尼龙,但力学性能往往不易得到保证.

本文以低代数的 PAMAM 分别与对苯二甲酸配制成母盐溶液,再以母盐溶液、己内酰胺、封端剂一起投入高压釜进行原位聚合,通过调节 PAMAM 在己内酰胺中的比例及改变不同的 PAMAM 代数得到不同样品,对各样品的力学性能,FTIR, MFI, DSC 非等温结晶行为进行了测试和表征.

1 实验原料

乙二胺,丙烯酸甲酯,甲醇,乙酸均从上海试剂公司采购,丙烯酸甲酯在合成前减压重蒸. 对苯二甲酸,己内酰胺为石家庄化纤公司提供.

2 高流动性尼龙 6 的合成

参考文献[14~16]的方法合成不同代数的 PAMAM,即 G1, G2 和 G3 PAMAM. PAMAM 再和对苯二甲酸按表 1 的配比先分别溶解在重蒸水中,再混合,在 50 ~ 80℃ 的水浴中反应 45 min,得到母盐溶液.

母盐溶液及各种尼龙 6 的详细投料见表 1.

Table 1 Detailed feed composition of different nylon 6 samples

Sample ^{a,b}	ϵ - Caprolactam (g)	Mother salt solution		
		PAMAM (g)	<i>p</i> -Phthalic acid (g)	Distilled water (g)
LPA6	700.0	0.0	0.0	21
BPAG1 * 0.5	694.4	3.5 (G1)	2.1	20 ~ 30
BPAG2 * 0.5	694.9	3.5 (G2)	1.6	20 ~ 30
BPAG3 * 0.5	695.6	3.5 (G3)	1.1	20 ~ 30
* BPAG2 * 0.3	696.9	2.1 (G2)	1.0	20 ~ 30
BPAG2 * 1.2	687.6	8.4 (G2)	4.0	30 ~ 40

^a All kinds of nylon 6 were made by *in situ* polymerization; ^b Acetic acid (2.1 g) was used as end capping agent for every sample.

母盐溶液,己内酰胺,封端剂(乙酸)一起投入到 2L 的高压反应釜中,多次以高纯氮充分置换釜内空气后分段升温. 先升温到 220℃,保温 2 h,再慢慢升温到 260 ~ 270℃,又保温 1 h. 整个过程压力不超过 0.8 MPa. 然后降压,以新鲜氮气置换以除掉水分,提高分子量,这样重复操作 3 ~ 6 次,缓慢降温至 230℃从釜底出料,在室温水浴中拉丝,经过切粒、沸水萃取、真空干燥(100℃),最后得到样品.

3 FTIR 分析

FTIR 显示(图 1),与线性尼龙相比较,高流动性尼龙 6 的 $\gamma(\text{N-H})$ 和 $2\delta(\text{N-H})$ 两处对应峰都发生了明显的蓝移. 这可能是少量树枝结构的存在破坏了尼龙 6 基体中相邻分子间的氢键作用而导致的^[17].

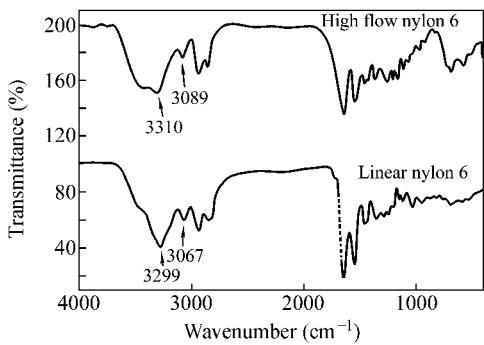


Fig. 1 FTIR spectra of linear and high flow nylon 6 (LPA6 and BPAG2 * 0.5)

4 分子量,流动性及力学性能

表 2 为各样品的特性黏度,分子量,熔体流动指数及力学性能测试结果.

Table 2 Test results for $[\eta]$, M , MFI and mechanical properties of LPA6 and high flow nylon 6

Sample	PAMAM content (wt%)	$[\eta]$ (dL·g ⁻¹)	M (× 10 ⁴)	MFI (g/10 min)	Tensile strength (MPa)	Elongation at break (%)	Izod impact strength (kJ/m ²)
LPA6	0	0.86	1.27	4.52	74	183	2.22
BPAG1 * 0.5	0.5 (1.0G)	0.70	0.97	7.93	74	150	2.58
BPAG2 * 0.5	0.5 (2.0G)	0.74	1.04	8.69	75	152	2.60
BPAG3 * 0.5	0.5 (3.0G)	0.75	1.06	7.95	74	115	2.75
BPAG2 * 0.3	0.3 (2.0G)	0.76	1.07	7.55	75	148	2.62
BPAG2 * 1.2	1.2 (2.0G)	0.52	0.66	17.27	65	180	2.45

显然,新型尼龙 6 流动性的显著改善不是分子量的降低,而是有尼龙 6 基体中含有枝化结构,枝化结构使尼龙 6 基体中相邻分子间的氢键作用遭到破坏^[17],分子间作用力减弱.同时,树枝单元的加入使尼龙 6 基体的断裂伸长率有不同程度的降低^[21].

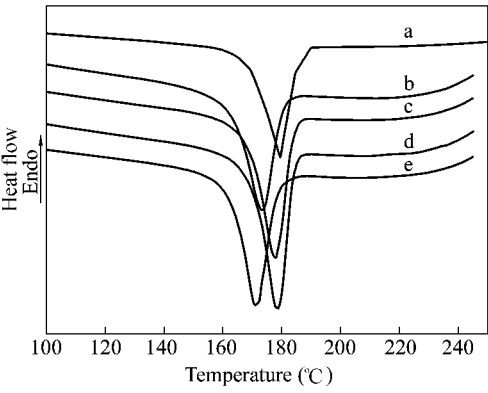


Fig. 2 Cooling scans of samples taken from LPA6 (a) and high flow nylon 6 : BPAG1 * 0.5 (b), BPAG2 * 0.5 (c), BPAG3 * 0.5 (d) and BPAG2 * 1.2 (e)

表 2 中的分子量,是利用 Mark-Houwink 方程式 $[\eta] = KM^\alpha$ ($K = 6.3 \times 10^{-4} \text{ dL} \cdot \text{g}^{-1}$, $\alpha = 0.764$) 进行计算得到的^[18].从表观上看,高流动性尼龙 6 的分子量都比纯尼龙 6 的分子量小,但谭惠民等认为,线形无规线团聚合物 α 为 0.7 左右,枝化聚合物 α 值低于 0.5^[19].对于样品 BPAG2 * 1.2,若改变其 α 值为 0.5,经计算得到分子量大于 6.8×10^5 若为 0.6,则分子量有 7×10^4 ,这从侧面证明了 PAMAM 枝化单元的存在使尼龙 6 的分子量增大了^[20].表 2 显示,对于树枝单元的含量较低 (0.3 wt% ~ 0.5 wt%) 的新型尼龙 6,拉伸强度没有减弱,缺口冲击强度增加了,而熔体流动却有了很大改善.

5 示差扫描热分析

图 2 为几种样品的非等温结晶曲线 (Netzsch STA 449C DSC) (at 10 K/min).显然,含树枝单元的高流动性尼龙 6 的峰宽比线性尼龙 6 都要宽些,而且随代数增加或含量的增多而增宽.图 2 也显示新型尼龙 6 的结晶曲线的结晶峰温度有不同程度的降低,晶体生长速率明显减慢^[22],这与这种新型尼龙 6 的高流动性是一致的.

以上研究表明,利用 PAMAM 母盐溶液与己内酰胺进行原位聚合,得到基体中含少量树枝单元的尼龙 6 新品种.对于树枝单元含量较低 (0.3 wt% ~ 0.5 wt%) 的新型尼龙 6,拉伸性能没有下降,缺口冲击强度增加,而熔体流动却显著得到改善.高流动性尼龙由于流动性好、成型周期短、降低能耗、增强产品外观等优点,具有很好的应用前景.

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in situ POLYMERIZATION AND CHARACTERIGATION OF HIGH FLUIDITY
NYLON 6 CONTAINING LOW CONTENT OF PAMAM UNITS

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Abstract A new strategy was developed for preparation of high fluidity nylon 6 on a large scale. Generation 1,2,3 (G1,G2,G3) polyamidoamine (PAMAM) dendrimers reacted with *p*-phthalic acid by equimolar terminal groups in water solutions, respectively, and mother salt solutions were then prepared. The high fluidity nylon 6 was prepared with suitable quantity of mother salt solution, end capping agent (acetic acid) and ϵ -caprolactam by *in situ* polymerization. By changing the quantity of mother salt solution or the generation of PAMAM dendrimers, different samples of high fluidity nylon 6 were obtained. Blue shifts were found for the peaks of NH (γ N—H and 2δ N—H) of the high fluidity nylon 6 compared with pure nylon 6 in the IR spectra. Compared with pure nylon 6, the samples of high fluidity nylon 6 with low content of PAMAM units (0.3 wt% ~ 0.5 wt%) had greater MFI, the value of MFI was improved about 70% ~ 90%. It was also found that there was a drastic increment in MFI when the content of PAMAM units in PA6 matrix increased from 0.5 wt% to 1.2 wt%, while the molecular weight of the high fluidity nylon 6 did not decrease. For the high fluidity nylon 6 with low content of PAMAM units (0.3 wt% ~ 0.5 wt%), the tensile strength did not decrease while the elongation at break decreased (ca. 20% ~ 35%), and the izod impact strength of different kinds of high fluidity nylon 6 increased. DSC thermograms of non-isothermal crystallization exhibited that the peak temperature of high fluidity nylon 6 was lower than that of pure nylon 6, and the peak of crystallization curve broadened comparing with the pure nylon 6 at the same crystallization condition, which broadened more with increasing the generation or the content of PAMAM units. Broader peak means the crystallization rate was decreased and the fluidity was improved, which benefits molding of small parts with thin walls or precision parts.

Keywords Nylon 6, High flowability, PAMAM dendrimers, *in situ* Polymerization