Synthesis and Characterization of Starch Grafted Biodegradable Polyester and Polyesteramide by Direct Polycondensation

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Abstract: Copolymers of starch grafted with poly (lactic-co-glycolic acid) and poly (lactic-co-glycolic acid-co-caprolactam) were prepared by direct polycondensation of soluble starch with lactic acid, glycolic acid and caprolactam in the presence of stannous chloride [$SnCl_2$]. The chemical microstructure of the resultant grafted copolymers was clarified by NMR spectroscopy and the thermal properties was investigated by differential scanning calorimetry (DSC) and thermogravimetric (TG) analysis.

Key words: Biodegradable; Starch; graft; Direct polycondensation
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Starch as biodegradable plastics for its nontoxic, natural abundance and low cost has been applied extensively. However, like most polysaccharides, the high hydrophilicity, poor processability and solubility in common organic solvents limited its wide applications. Therefore, the modification of starch, physically and chemically, has been extensively studied.

Chemical modifications of starch, including chemical derivation and graft copolymerization, are efficacious methods to improve the properties of starch. Graft copolymerization, as a rational approach of chemical modification, has been extensively used in the modification of starch. In fact, owing to the environmental and ecological concerns, researches on biodegradable compositions based on degradable polyester grafted starch-like polysaccharides have been focused on for decades. Biodegradable polyesters, such as polycaprolactone (PCL) and poly (lactic acid) (PLA) can be grafted by ring-opening polymerization[1] or coupled reaction[2—3]. But these methods were uneconomical and environmentally unfriendly.

In this paper, two kinds of the starch graft hydroxyl acid and amino acid copolymers were synthesized by direct polycondesation. This organic solvent-free reaction process gives an economical, facile and environmentally friendly method for the preparation of biodegradable modified starch.

1 Syntheses

Soluble starch, the aqueous solution of lactic acid, glycolic acid and caprolactam were added to a 250 mL three-necked flask equipped with a mechanical stirrer and vacuum pump system. The temperature of the reaction system was thermostated by a temperature controlling system. Starch was first gelatinized at 75 ℃. When most of water was drawn out, a stannum containing catalyst (0.3 wt% of total amount of the reactants) was added to the flask. The graft copolymerization was proceeded at 120 ~ 170 ℃ under vacuum (0.085 MPa) for predetermined time.

Tab.1 Synthesis of starch graft PLGA and PLGC

Entry	Weight/g				Temperature /℃
	Starch	Lactic acid	Glycolic acid	Caprolactam	
S1	4.5	4.5	4.5	—	120
S2	2.0	5.5	5.5	—	150
S3	1.0	6.0	6.0	—	170
S4	3.0	3.0	3.0	6.0	170
S5	3.0	3.0	3.0	4.0	170
S6	3.0	3.0	3.0	2.0	170

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2 Results and discussion

2.1 The assignment of the characteristic resonance

The ^{1}H-NMR spectra of starch-g-PLGA and starch-g-PLGC copolymers are shown in Fig. 1. We assigned the proton signals in the NMR spectrum of starch-g-PLGA as quoted in Table 2.

Tab. 2 Chemical shift assignments for ^{13}C and ^{1}H-species of St-g-PLGA

^{13}C assignment	Chemical shift/10^{-6}	^{1}H assignment	Chemical shift/10^{-6}	C and H species
Ca	174.1, 169.8, 169.3, 169.1	--	--	-C=O (LA)
Cb	172.2, 171.2, 167.2	--	--	-C=O (GA)
Cc	65.8, 65.7, 65.5	Hc	5.20, 4.21	-CH (LA)
Cd	61.2, 60.8, 60.1	Hd	4.81	-CH_2 (GA)
Ce	20.4, 16.5, 16.6	He	1.22-1.29, 1.41-1.46	-CH_3 (LA)
C1	128.1, 125.5	H1	4.91	O-CH-O (St)
C2	69.2, 69.0	H2	4.60-4.66	-CH- (St)
C3	73.1, 71.6	H3	3.50	-CH- (St)
C4	79.3, 79.0, 78.7	H4	3.70	-CH- (St)
C5	68.7, 68.3	H5	3.80	-CH-CH_2 (St)
C6	59.5, 59.3	H6	3.90, 4.10	-CH_2 (St)
--	--	H7	5.50	-OH

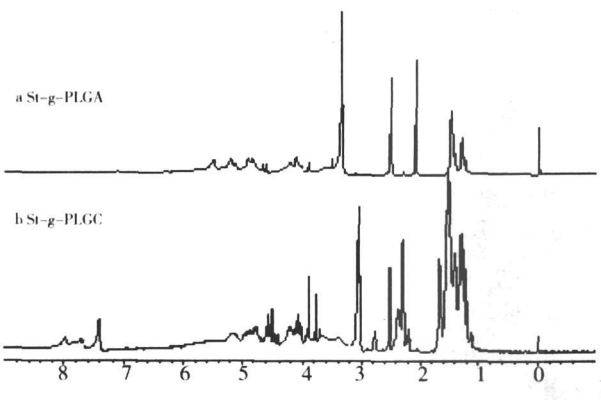

Fig. 1 ^{1}H-NMR spectra of starch-g-PLGA and starch-g-PLGC

2.2 The thermal properties of the copolymers

We have investigated the thermal stability (temperature of thermal decomposition, T_d) and glassy translation temperature (T_g) of copolymers by thermogravimetric analysis (TGA) and differential scanning calorimetric (DSC) measurements, respectively.

Tab. 3 Thermal properties of starch-g-PLGA and starch-g-PLGC

T(℃)	Starch	S1	S2	S3	S4	S5	S6
T_d	271.5	235	245	269.8	150	225	210
T_g	--	27	23	15	-15	-6	3

Compare with starch, the TG data and the DSC data clearly demonstrates that temperature of thermal decomposition and the melt point of these copolymers are lower.

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切削大塑性变形制备纳米材料

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摘 要: 长期以来, 切屑都被看成是金属切削过程中产生的废物。最新研究表明在一定切削条件下形成的切屑几乎全部为纳米结构材料。首先分析了切削加工中材料的塑性变形特征, 然后将切削大塑性变形制备纳米结构材料工艺与其他传统的剧烈塑性变形工艺进行比较, 发现切削法具有工艺简单, 价格低廉, 生产效率高, 对高强度材料同样适用等优点, 同时还可以减少切屑回收过程对环境造成的污染。

关键词: 切屑回收; 金属切屑; 纳米材料; 切削
中图分类号: TG501

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直接缩聚法合成淀粉接枝可降解聚酯和聚酯酰胺及其表征

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摘 要: 以可溶性淀粉、乳酸、乙醇酸和己内酰胺为原料在氯化亚锡催化下直接缩聚制备得到了淀粉接枝乳酸-乙醇酸共聚物及淀粉接枝乳酸-乙醇酸-己内酰胺共聚物。用核磁共振 (NMR)、差热 (DSC) 及热重 (TG) 分析分别对产物的结构和热性能进行了表征。

关键词: 生物可降解; 淀粉; 接枝; 直接缩聚
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