Study on the Copolymerization of Grafting PVP onto PHBV

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Abstract: The orthogonal array design method was adopted to optimize reaction conditions of grafting poly (N-vinylpyrrolidone) (PVP) onto poly (3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) backbone in chlorobenzene. The results showed that the weights of N-vinylpyrrolidone (NVP) and benzoyl peroxide (BPO), reaction temperature were the highly significant factors to affect the grafting ratio (GR%). The 90% confidence interval on the estimator of GR% under the optimized copolymerization conditions was (9.83 ± 1.14)% which was in accordance with the experiment result (10.48%).

Key words: graft copolymerization; orthogonal array design; grafting ratio; PHBV; PVP
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Recently, a biodegradable thermoplastic polymer, poly (hydroxybutyrate-co-hydroxyvalerate) (PHBV), is attracting more and more interests in research and industry fields[1]. Poly (N-vinylpyrrolidone) (PVP) has been widely used as medical additives or polymeric modifiers[2-5]. In this study, PVP was originally grafted onto PHBV to synthesize a new novel biomaterial which would combine the advantages of PHBV substrate and PVP groups. The orthogonal array design method was adopted to optimize the reaction conditions for obtaining the highest grafting ratio.

1 Experiments

1.1 Materials

PHBV (Tian'an Bioproducts Ltd. Co., China) was recrystallized from ethanol. N-vinylpyrrolidone (NVP), purchased from Fluka, was treated with active carbon sorption to get rid of the inhibitor before using. Benzoyl peroxide (BPO), obtained from Shanghai Zhongli Chemical Factory, was recrystallized from methanol. Chlorobenzene and ethanol supplied by China Medicine Groups, were used as received.

1.2 Reaction of grafting PVP onto PHBV

The PHBV powder with the dried weight of 2.5 g was completely dissolved in 25 mL chlorobenzene in a three-neck flask and the given weights of NVP monomer and BPO initiator were added to it, then the solution was heated up to a chosen temperature under nitrogen atmosphere. The selected factors and levels in experiment are shown in Tab. 1. After a chosen period of reaction, the 100 mL ethanol was poured into the solution with stirring. Then the formed precipitates were filtered and washed for several times. The dried weight of products (W) should be higher than 2.5 g. From the increased weight, the grafting ratio (GR%) could be estimated as the following equation:

$$GR\% = \frac{W - 2.5}{2.5} \times 100 \quad (1)$$

Tab. 1 Selected factors and levels in the experiment

Factors	Levels			
	1	2	3	4
A Reaction temperature/℃	100	110	120	130
B Reaction time/h	1	2	3	4
C BPO weight in feed/g	0.2	0.4	0.6	0.8
D NVP weight in feed/g	2.5	5.0	7.5	10.0

2 Results and discussion

Tab. 2 shows the $L(4^5)$ orthogonal array design and results of the experiment. Tab. 3 shows the statistic analysis of experimental results. From the Tab. 3, it can be concluded that the weights of NVP and BPO in

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Tab. 2　$L_{16}(4^5)$ orthogonal array design and results

Exp. No	A	B	C	Error	D	GR/%
1	1	1	1	1	1	1.23
2	1	2	2	2	2	4.56
3	1	3	3	3	3	8.81
4	1	4	4	4	4	8.34
5	2	1	2	3	4	8.78
6	2	2	1	4	3	4.89
7	2	3	4	1	2	5.26
8	2	4	3	2	1	2.74
9	3	1	3	4	2	6.98
10	3	2	4	3	1	2.43
11	3	3	1	2	4	6.10
12	3	4	2	1	3	8.14
13	4	1	4	2	3	4.75
14	4	2	3	1	4	6.89
15	4	3	2	4	1	1.25
16	4	4	1	3	2	1.09

feed, reaction temperature are the highly significant factors to affect the GR/%, and the optimal copolymerization conditions are $A_3B_1C_3D_4$, i.e. reaction temperature at 120℃, reaction time of 1 h, weight of BPO 0.6 g, and weight of NVP 10 g. According to basic principles of statistics, the 90% confidence interval on the estimator of GR ((9.83±1.14)%) at the optimal copolymerization conditions can be calculated. GR/% increased with increasing NVP weight in feed all the time, so the experiments at higher NVP weight should be further evaluated.

Tab. 3　Data structure for storing packet decoded information

Factors	Estimator of factorial effect				Degrees of freedom	Mean square
	1	2	3	4		
A	0.60	0.28	0.77	−1.65	3	4.98
B	0.30	−0.45	0.22	−0.07	3	0.45
C	−1.82	0.54	1.23	0.05	3	6.74
D	−3.23	−0.67	1.51	2.39	3	25.11
Error					3	0.65

Fig. 1 shows the effects of NVP weight in feed on GR/% (other reaction conditions were $A_3B_1C_3$). It can be seen that GR/% increased with increasing NVP weight, reaching to its maximum value (10.48%) at NVP weight of 10 g, and then decreased. The highest GR/% value is in accordance with the estimator.

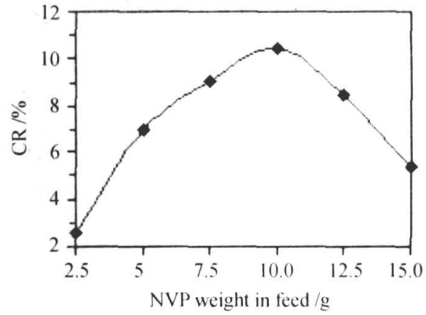

Fig. 1　Effects of NVP weight in feed on GR

3　Conclusions

PVP groups were successfully grafted onto PHBV backbone in chlorobenzene using BPO as a initiator. The weights of N-vinylpyrrolidone (NVP) and benzoyl peroxide (BPO), reaction temperature were the highly significant factors to affect the GR/%. The optimal copolymerization conditions were reaction temperature at 120℃, reaction time of 1 h, weight of BPO 0.6 g, and weight of NVP 10 g. The grafted PHBV with different GR/% can be easily obtained by varying the NVP weight in feed.

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PVP接枝 PHBV的研究

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摘　要：采用正交实验设计优化聚乙烯吡咯烷酮 (PVP) 与聚羟基戊酸－co－羟基丁酸共聚酯 (PHBV) 在氯苯溶液中的接枝反应工艺。结果表明：乙烯基吡咯烷酮 (NVP) 与过氧化二苯甲酰 (BPO) 用量，反应温度显著影响接枝率 (GR/%)。在优化的反应工艺条件下，接枝率的置信度为 90%的置信区间是 (9.83±1.14)%，该值与实验结果 (10.48%) 一致。

关键词：接枝共聚；正交实验设计；接枝率；PHBV；PVP

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