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Fluorocarbon modified chitin and chitosan
I. Synthesis and characterization of perfluorocarbonyl chitin

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SUMMARY: The esterification reaction of chitin with perflurocarboxylic acid was studied in methanic acid or perfluorocarboxylic acid as solvent. A series of substituted derivatives of trifluoroacyl. perfluorobutyric and perfluorooctanoyl chitin were synthesized. The properties of these chitin derivatives were investigated.

Introduction

Since energy crisis after early of 70's, the regeneration of natural resources has been given much more attention and extensive interest, for example, the investigation of modification on cellulose and chitin. The chemical structure of both cellulose and chitin are similar. Chitin is an essential composition in a lot of elementary animals such as shell of shrimp, crab, insect and anthropods etc., there are more than billion tons natural-synthesize chitin every year in world. Therefore the research of modified chitin is very attractive at the present time[1]. The acrylating reactions of chitin are the most studied reactions in chitin chemistry. The solubility of modified chitin in organic solvent is improved greatly by introducing various alkyl or aromatic acyl group onto the backbone of chitin[2,3]. There is no research work about the modified chitin by substitution of fluorocarbon compound. In this paper, the various length chain of perfluorocarboxy acid were introduced onto the backbone of chitin and the reaction and the properties of fluorocarbon modified chitin derivations were studied.

Experimental

Chitin was purchased from Tokyo Kasei Kogyo Co. Ltd. powdered to 50 mash before use. The synthesis reaction as shown below:

I. Preparation of trifluoro acyl chitin:

Chitin powder 1.0g was added to the mixture of methyl sulphonic acid and trifluoro acetic acid (V/V=7ml/3ml) or trifluoro acid (10ml) in a 50ml flask. The reaction was carried out with magnetic stirrer at 5°C for various hours until the mixture was became a

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gel and then over night at -20 °C, ice was added into the flask , then stirred and separated by centrifuge, the solid was washed by ethanol and ether, then separated again by centrifuge. The solid was dried in vacuum oven at room temperature.

II. Preparation of perfluoro butyric (or octanoyl) chitin

Chitin powder 1.0g was added to the mixture or methanoic acid (7ml) and perfluoro butyric acid or perfluorooctanoic acid in 50ml flask. The reaction was carried out with magnetic stirring at 5°C for various hours. The treatment of reaction mixture was same as I.

Results and Discussion

I. Esterificate reaction and choice of solvent :

The chitin is not dissolved in most organic solvent, because the hydrogen bond is strong in chitin. The methylsulphonic acid or mixture of trifluoro acetic acid and dichrolo ethane were used usually as solvent. The degradation of chitin effected by temperature have and studied in a solution of methyl sulphonic acid by Kaifu[2] , could be avoided at lower temperature. Considering of the difficulty of processing the film of the modified chitin using the methyl sulphonic acid as solvent, the esterification reaction of chitin with fluorocarbon compound was carried out using trifluoroacetic acid both as solvent and substrate. The results were listed in Table 1. As shown in Table 1, the esterificate reaction was successful using the trifluoro acetic acid as both of the solvent and the substrate. The substitution of trifluoro acyl was also effected by reaction time. The results were listed in Table 2. The maximum substitution was at 8hrs.

II. Esterificate reaction of chitin with various length of perfluoro carboxy acid:

The perfluorobutyric acid and perfluoro octanoic acid were used instead of trifluoroacetic acid for esterificcate reaction of chitin. The results were listed in Table 3. According to these results, the reactivity of perfluoro-carboxy acid decreased with increasing the length of fluorocarbon chain.

As Figure 1. shows the IR spectra of various degree of substitution (DS) of perfluorobutyric chitin compared to IR spectra of chitin, 1760-1790cm^{-1} is typical peak of F—C bond. The intensity of these peaks increased with increasing DS.

The properties of these derivation was studied and it was found that the biodegradable property was very similar as chitin or chitosan, the research are in progress.

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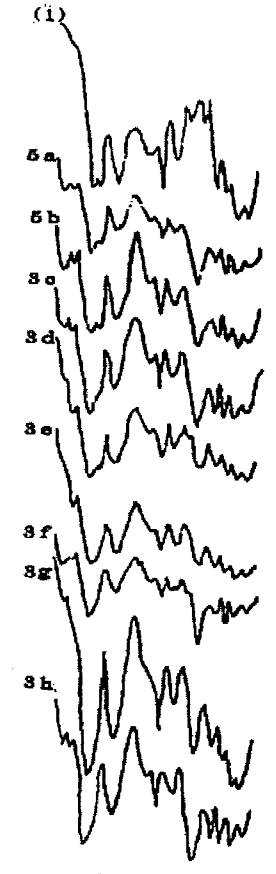

Fig. 1 IR Spectra of tri-fluoro acyl chitin and chitin

(1) Pure chitin and 5a – 5b and 3c-3h in Table 2

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Table 1. Effect of Solvent to the Degree of Substitution

Reaction time(hr)	CF_3COOH(ml)	CH_3SO_3H(ml)	F wt.(%)	(D.S) Degree of Substitution *
7	3	7	11.64	0.52
7	10	0	11.26	0.50

Table 2. Esterificate Reaction of Trifluoro acetic acid and Chitin

No.	Reaction time(hr)	F wt.(%)	D.S.*
5a	3	5.70	0.23
5b	4	5.82	0.23
3c	5	5.87	0.23
3d	6	11.02	0.48
3f	7	11.26	0.50
3g	8	11.95	0.53
3h	9	11.19	0.49
	10	11.09	0.49

Table 3. Esterificate Reaction of Various Length of Chain of Perfluoro alkyl acid and Chitin

No.	Various length chain of perfluoro alkyl acid	F wt.(%)	D. S.*
1	CF_3COOH	11.95	0.53
2	$CF_3(CF_2)_2COOH$	21.83	0.49
3	$CF_3(CF_2)_6COOH$	24.29	0.26

* D. S. = F%×203.19/(57.00-F%×96.01)

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