Amino-Dealkoxylation of HM Citruc Pectin with *n*-Alkylamines: A Kinetic Study

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Abstract: Pectins are plant polysaccharides that are widely used in food industry. Chemical modification of pectins influences their technological properties. Amidated pectins are important pectin derivatives with good gelling properties at low-sugar conditions. The common method of pectin amidation is ammonolysis of methyl ester groups of highly methoxylated (HM) pectins in heterogeneous reaction with ammonia in methanol. Amino-dealkoxylation (aminolysis) of HM pectin with primary amines leads to the formation of *N*-alkylpectinamides. The reaction yield of aminolysis depends on reaction time, temperature and the pectin/alkylamine ratio. The reaction of HM citrus pectin (type XSS, Danisco) with five chosen *n*-alkylamines (*n*-butylamine, *n*-hexylamine, *n*-octylamine, *n*-dodecylamine and *n*-octadecylamine) was carried out in *N*,*N*-dimethylformamide at 20°C (*n*-butylamine, *n*-hexylamine, *n*-octylamine) and at 50°C (all the amines) for 1–9 days. Obtained results can be applied to prepare *N*-alkylpectinamides of predicted DA varying the reaction time at the same reaction conditions (temperature, pectin/alkylamine ratio).

Keywords: *N*-alkylpektinamides; HM citrus pectin; amino-dealkoxylation (aminolysis)

INTRODUCTION

Pectin is a component of fruit and vegetables, and it is an excellent jellying agent for food industry. Pectin is also known as a cholesterol-reducing dietary fibre [1, 2]. Pectin is totally degraded in the proximal colon owing to fermentation by intestinal microorganisms. Digestible pectins cannot prevent colorectal carcinomas and inflammations, which are developed in the distal colon. Chemical modification of pectin, however, may decrease its availability for intestinal microorganisms. Pectin has not been often used for preparation of derivatives for food industry. An introduction of non-polar residues increases hydrophobic character of pectin macromolecules. It has been reported earlier that alkyl esters of pectin and pectic acid adsorb bile acids, fat and cholesterol [3, 4]. The chemical modification of highly methylated (HM) pectin (amidation, trans-esterification) is relatively easy due to the presence of natural methylester groups in pectin macromolecules. *N*-Alkylpectinamides have some advantages in comparison with other alkylated pectin derivatives: their preparation does not require extreme conditions, and the amide bond is sufficiently resistant to chemical hydrolysis. Yields of *N*-alkylamides prepared by reaction of pectin with aliphatic non-branched amines are relatively high [5, 6]. It has been reported that highly substituted *N*-octadecylpectinamide can be used as hydrophobic sorbent due to its affinity to non-polar molecules (*n*-alkanes, *n*-alkylbenzenes and polyaromates) [7]. For technological applications it is necessary to obtain *N*-alkylpectinamides of predicted degree of amidation (DA). In this paper we describe the kinetic study of amino-dealkoxylation (aminolysis) of HM pectin with five chosen *n*-alkylamines at various reaction conditions.

EXPERIMENTAL

The reaction of HM citrus pectin (type XSS, Danisco) with five chosen *n*-alkylamines (*n*-butylamine, *n*-hexylamine, *n*-octylamine, *n*-dodecylamine and *n*-octadecylamine) was carried out in heterogeneous system in *N*,*N*-dimethylformamide (DMF) or in methanol medium. The reaction was carried out under continuous mixing at 20°C (*n*-butylamine,

n-hexylamine, *n*-octylamine) and at 50°C (all the amines). The solids were washed by the medium solvent at appropriate temperature to remove free amine and then washed with 0.1 mol/ l-1 HCl in the ethanol-water (1:1 v/v) mixture to convert ionised carboxylic groups into protonated form. This step is necessary to hydrolyse alkylammonium salt that can be formed in the reaction of HM pectin with alkylamines. Finally, the products were washed by 80% aqueous ethanol, filtered and dried at 60°C. The degrees of amidation (DA) of the products were calculated based on diffusion reflectance FT-IR spectra. The spectra were measured on Nicolet 740 (Nicolet Analytical Instruments, USA) spectrometer with DCT 680, 256 scans were accumulated with a spectral resolution of 4.0 cm^{-1}. All graphs were made using Origin 6.0 software (Microcal Origin, USA).

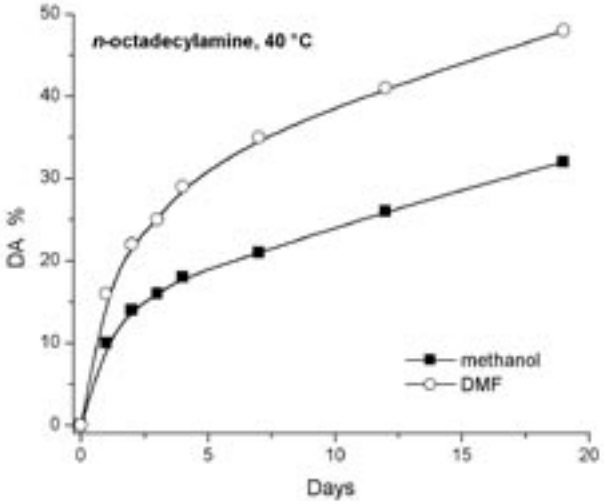

Figure 1. Time dependence of DA values (%) during amidation of HM citrus pectin with *n*-octadecylamine in methanol and DMF medium

RESULTS AND DISCUSSION

The main task of this work was to check how various factors, i.e. reaction medium, temperature, pectin/amine mass ratio and alkyl length in amine molecule, influence amino-dealkoxylation process. Time dependence curves for DA values of *N*-octadecylpectinamines obtained by amidation in methanol and DMF medium are shown in Figure 1. It is clear that amidation is much more effective in DMF than in methanol. As good suspending agent [8], DMF was applied before an addition of *n*-alkylamine to prepare gentle suspense of HM pectin. This improvement led to significant decreasing of reaction time in comparison with the reaction in methanol medium [5, 6]. The reaction with liquid amines (*n*-butylamine, *n*-hexylamine and *n*-octylamine) was made at two temperatures: 20°C and 50°C during 7 days. The DA values of obtained products are shown in Figure 2a. All the derivatives prepared at 20°C demonstrate DA values up to 10%, whereas corresponding values of *N*-alkylpectinamines prepared at 50°C are 3–5.5 times higher. Therefore, higher temperatures are useful for preparation of highly substituted products at relatively short terms. On the other hand, if

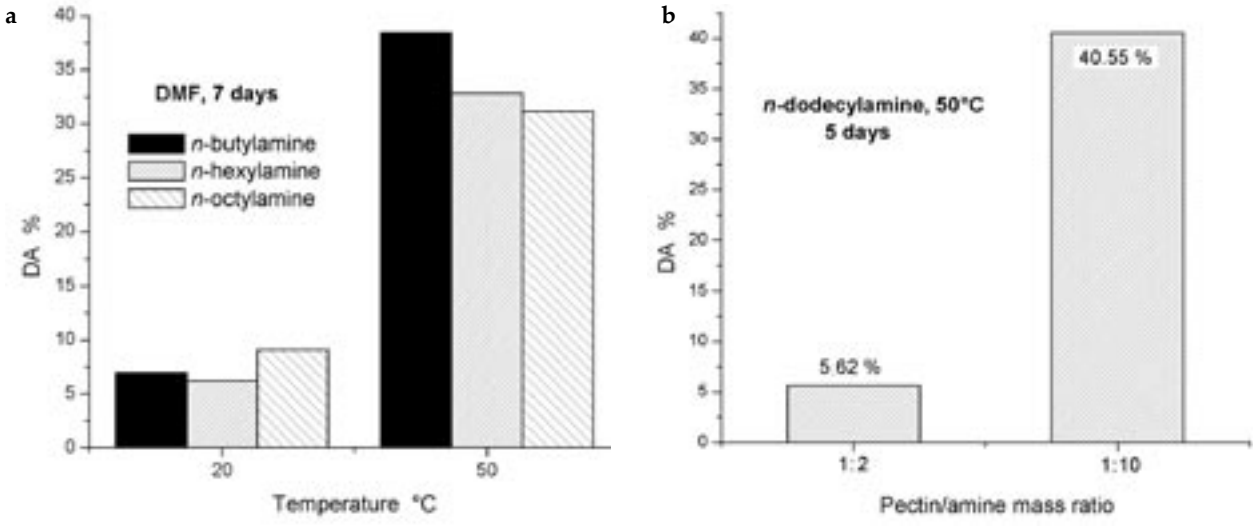

Figure 2. Influence of reaction temperature (a) and pectin/amine mass ratio (b) on the DA value (%) of *N*-alkylpectinamides

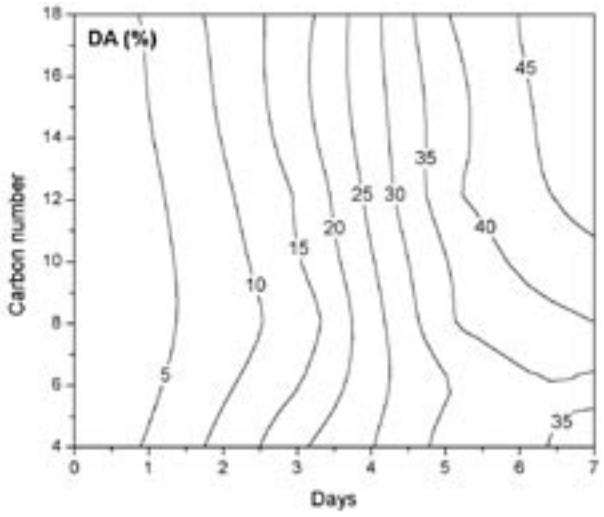

Figure 3. Contour map of DA values (%) of *N*-alkylpectinamides obtained by reaction of HM citrus pectin with five *n*-alkylamines at 50°C for 3, 5 and 7 days

the reaction temperature is too high (> 60°C), the degradation of polysaccharide may occur. Another important factor of amino-dealkoxylation is the pectin/amine mass ratio. It is necessary to use an excess of amine reagent to obtain highly substituted products. Two *N*-dodecylpectinamines prepared at two pectin/amine mass ratios (1:2 and 1:10) were obtained and the DA values of these derivatives are shown in Figure 2b. The former reagents' ratio led to significantly less effective amidation than the latter one. The structure of *n*-amine molecule, i.e. the number of carbon atoms in alkyl group, also influences the process of pectin amidation. We would like to analyse a role of this structural factor in the reaction. For this purpose, amino-dealkoxylation of HM pectin with five chosen *n*-amines was made at the same conditions (DMF; pectin/amine mass ratio 1:10; 50°C; 3, 5 and 7 days). Obtained results are summarised in Table 1. The contour map (Figure 3) illustrates how the DA values of the products depend on the reaction time (*x*-axis) and the number of carbon atoms in alkyl group (*y*-axis). It was found, surprisingly, that *n*-amine reagents with longer alkyls seems to be more effective amidation agents at higher reaction terms. This phenomenon could be explained by hydrophobic interactions between alkyls of amine molecule and *N*-alkylamide groups attached to polysaccharide. These interactions may support further amidation in the case of longer amines.

Table 1. DA values (%) of *N*-alkylpectinamides obtained by reaction of HM citrus pectin with five *n*-alkylamines at 50°C for 3, 5 and 7 days

Amine reagent	Reaction time, days		
	3	5	7
n-Butylamine	20	33	38
n-Hexylamine	15	30	33
n-Octylamine	12	36	41
n-Dodecylamine	16	40	48
n-Octadecylamine	18	42	50

CONCLUSIONS

Amino-dealkoxylation of HM citrus pectin with *n*-alkylamine is complex heterogeneous process depending on reaction conditions (medium, temperature, reagents' ratio) and the amine structure. The results obtained in this study can be applied to prepare *N*-alkylpectinamides of predicted DA varying the reaction time at the same reaction conditions. Further experiments will be made to confirm our assumption about a role of structural factor in amidation of HM pectin.

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