

Dextrine-modified chitosan marine polymer coatings

TOSHIFUMI SUGAMA, SHEILA MILIAN-JIMENEZ

Energy Efficiency and Conservation Division, Department of Applied Science, Brookhaven National Laboratory, Upton, NY 11973, USA

E-mail: sugama@bnl.gov

In trying to modify partially acetylated chitosan (CS) marine polymers ground from crab or shrimp shells for use as environmentally benign water-base coatings for aluminum (Al) substrates, CS was dissolved in a solution of HCL acid, and then mixed with corn starch-derived dextrine (DEX) containing Ce nitrate as oxidizing agent in aqueous medium. This blend of polysaccharides was deposited on Al surfaces by a simple dip-withdrawing method, and then heated at 200 °C to transform the liquid layer into a solid film. The solution → solid phase transition provided the changes in the molecular conformation of CS and DEX; the former was transformed into deacetylated poly(D-glucosamine) and the latter referred to the formation of Ce-complexed carboxylate fragments. Furthermore, the chemical reactions between the NH₂ groups in deacetylated CS and the carboxylate fragments led to the creation of amide linkages that served in grafting DEX fragments onto the CS. Such fragment-grafted CS polymer coating films deduced from the proper proportions of CS to DEX offered great film-forming performance, low susceptibility to moisture, and low ionic conductivity, conferring a salt-spray resistance of 720 hours.

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1. Introduction

In attempting to replace coating systems containing environmentally harmful ingredients, such as volatile organic compound (VOC) and toxic chromium and lead compounds, by environmentally acceptable water-based ones, our previous work [1, 2] focused on seeking ways to modify and design non-toxic natural polysaccharide polymers from the potato-starch and corn-starch derived dextrine as renewable agricultural resource. The modifications were made in the following two ways: One way involved reconstituting an oxidation-derived fragmental polysaccharide structure by Ce; the other way was by grafting synthetic water-soluble polymers, such as polyorganosiloxane and polyacrylamide, onto the polysaccharide. The former method employed a two-step reaction. The first step consisted of fragmentating the polysaccharide structure by incorporating Ce nitrate (CAN), as a chemical oxidizing agent, into the polysaccharide solution; this was followed by thermal oxidation in the presence of atmospheric oxygen. The second step was to assemble water-insoluble Ce-complexed conformations by the interactions between the Ce ions liberated from CAN and fragments containing oxygen functional derivatives such as C=O and COO⁻. Using the latter method, the grafting was accomplished by ether- and amide-linkages formed through the condensation reactions between the silanol end groups in polyorganosiloxane or the amine pendent groups in the polyacrylamide, and the OH groups of glycol in the polysaccharide. These

modifications successfully resolved the following five undesirable problems that arose when the polysaccharide was directly applied as a protective coating without any molecular modifications to the metal substrates; there were (1) the settlement and growth of microorganisms in its aqueous solution, (2) the high susceptibility of films to moisture, (3) the poor chemical affinity of films for Al surfaces, (4) the weak adherence to polymeric topcoatings, and (5) the biodegradation of films caused by fungal growth. There was no doubt that such modifications significantly enhanced the potential of polysaccharide for use in corrosion-protective coatings.

As part of our ongoing research aimed at developing an uniform, continuous hydrophobic natural polymer film that adequately protects aluminum (Al) substrates against corrosion, we next focussed on assessing the ability of chitosan [CS, poly(D-glucosamine)] ground from the crab or shrimp shells, to mitigate corrosion of Al. The CS, which is a family of polysaccharides, is well known as a low cost, renewable marine polymer, and is produced at an estimated amount of one billion tons per year [3]. However, an undesirable property of CS as the corrosion-mitigating coating films is that it absorbs a large amount of moisture in an atmospheric environment, and then forms a hydrogel [4]. Thus, the emphasis of current study centered on modifying the molecular structure of CS with corn-starch derived dextrine [DEX, poly(D-glucose)] to fabricate a material with a low susceptibility to moisture. The DEX-modified and unmodified CS polymers then were

investigated to gain information on their usefulness as water-based corrosion-preventing primer coatings for Al substrates. The factors to be investigated included changes in molecular configuration, thermal behavior, susceptibility to moisture, morphological features, and surface chemistry of films with different proportions of CS to DEX. The data obtained were integrated and correlated directly with the ability of these coating films to inhibit corrosion of Al.

2. Experimental

2.1. Materials

Chitosan (CS) with a degree of deacetylation of 75 to 85%, supplied by Sigma-Aldrich Fine Chemicals Co., was a coarse particle ground from crab or shrimp shells. Dextrin (DEX) fine powder derived from corn-starch was made by INC Biomedical, Inc. Cerium(IV) nitrate hexahydrate [CAN, $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$], obtained from Alfa, was used as the oxidizing agent. Hydrochloric acid (HCL, 37% in water) was employed to enhance CS's solubility in water. Two aqueous solutions, 1 wt % CS and 1 wt % DEX, were separately prepared before they were blended. The former solution was made by agitating a mixture of 1 g CS, 1 g HCL, and 98 g deionized water for 3 hours at 90 °C. The latter one was prepared in the following way: First, 1 g DEX was added to 99 g deionized water at 70 °C, and mixed by a magnetic stirrer for 2 hours. Then, it was allowed to stand for 24 hours at room temperature, before incorporating CAN of 0.2% by weight of the total DEX solution into it. The seven mix formulations for these DEX-modified CS solutions were designed in this study; there were the CS/DEX ratios of 100/0, 90/10, 70/30, 50/50, 30/70, 10/90, and 0/100, by weight. The lightweight metal substrate was a 6061-T6 aluminum (Al) sheet containing the following chemical constituents; 96.3 wt % Al, 0.6 wt % Si, 0.7 wt % Fe, 0.3 wt % Cu, 0.2 wt % Mn, 1.0 wt % Mg, 0.2 wt % Cr, 0.3 wt % Zn, 0.2 wt % Ti, and 0.2 wt % other elements.

2.2. Coating technology

The coating film was deposited on the Al surfaces in the following sequence: First, to remove surface contaminants, the Al substrates were immersed for 20 min at 80 °C in an alkaline solution consisting of 0.4 wt % NaOH, 2.8 wt % tetrasodium pyrophosphate, 2.8 wt % sodium bicarbonate, and 94.0 wt % water. The alkali-cleaned Al surfaces were washed with deionized water at 25 °C, and dried for 15 min at 100 °C. Next, the substrates were dipped into a soaking bath of film-forming solution at room temperature, and withdrawn slowly. The wetted substrates were then heated in an oven for 120 min at 150 or 200 °C, to yield thin solid films.

2.3. Measurements

The thickness of the DEX-modified and unmodified CS films deposited on the Al surfaces was determined using a surface profile measuring system. Differential scanning calorimetry (DSC) gave information on

the enthalpy of the first endothermic phase transition of modified and unmodified CS polymers. DSC was run using the non-isothermal method at a constant rate of 10 °C/min over the temperature range of 25 to 300 °C. The molecular configuration and conformation of 150°- and 200°-treated polymers was investigated by Fourier-transformation infrared (FT-IR) and X-ray photoelectron spectroscopy (XPS). The contact angle was measured by dropping water onto the polymer film surfaces to determine the extent of susceptibility of their surfaces to moisture. The values of contact angle were measured within the first 20 sec after dropping it onto the surfaces. Information on the surface morphology, texture, and film-forming performance of the coatings deposited onto the Al was gained by Scanning Electron Microscopy (SEM). AC electrochemical impedance spectroscopy (EIS) was used to evaluate the ability of the coating films to protect the Al from corrosion. The specimens were mounted in a holder, and then inserted into an electrochemical cell. Computer programs were prepared to calculate theoretical impedance spectra and to analyze the experimental data. Specimens with a surface area of 13 cm² were exposed to an aerated 0.5 M NaCl electrolyte at 25 °C, and single-sine technology with an input AC voltage of 10 mV (rms) was used over a frequency range of 10 kHz to 10⁻² Hz. To estimate the protective performance of coatings, the pore resistance, R_p , (Ω cm²), was determined from the plateau in Bode-plot scans that occurred at low frequency regions. The salt-spray tests of the coated Al panels (75 mm × 75 mm, size) were performed in accordance with ASTM B 117, using a 5 wt % NaCl solution at 35 °C.

3. Results and discussion

3.1. DEX-modified CS polymers

Before identifying the reaction products yielded by the chemical interactions between DEX and CS at 200 °C, we investigated the changes in chemical conformation of the CS itself at 150 and 200 °C, by FT-IR. In this study, the samples were prepared in accordance with the following method: First, a 200 g CS solution denoted as CS/DEX ratio of 100/0 was poured into glass test tubes, and then left for 24 hours in an air oven at 150 and 200 °C to form the solid polymers; Second, these polymers were ground to a particle size <0.074 mm for FT-IR exploration. Fig. 1 gives the FT-IR spectra for these samples over the frequency range from 1800 to 1000 cm⁻¹. For comparison, the spectrum of "as-received" CS powder, as the reference sample, is also illustrated in this figure. The CS reference sample (a) had absorption bands at 1654, 1549, and 1314 cm⁻¹, revealing the amide I (stretching vibration of carbonyl group, C=O), amide II (bending vibration of secondary amine group, NH), and amide III (stretching vibration of C-N bond) in the secondary amide groups, respectively, at 1590 cm⁻¹ which can be ascribed to the N-H bending mode in the primary amine, NH₂, groups, at 1419 and 1372 cm⁻¹, reflecting the C-H bending modes of the methy and methylene, and also at 1149, 1078, and 1026 cm⁻¹, corresponding to the stretching

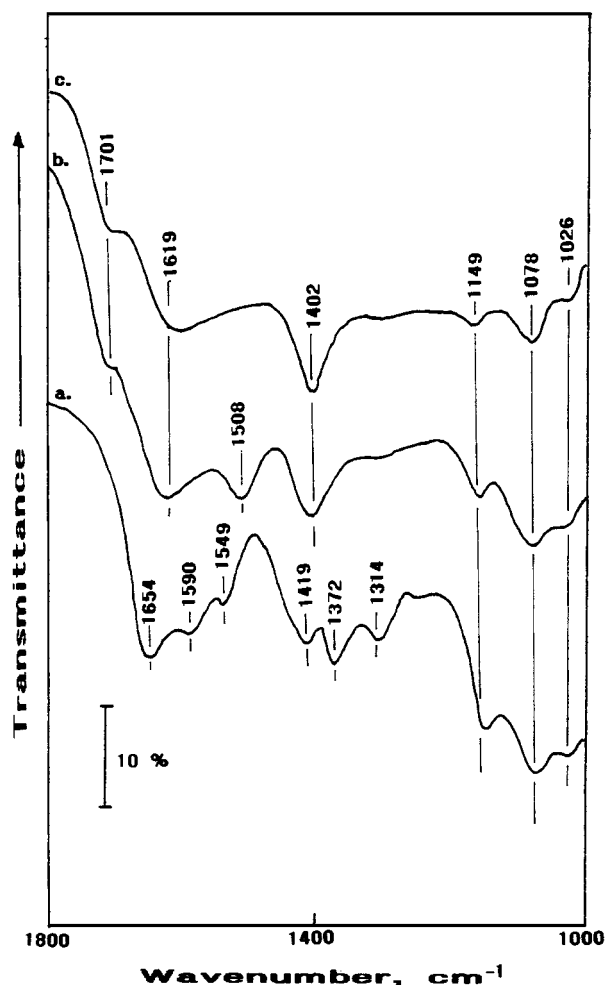
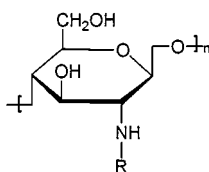


Figure 1 FT-IR absorption spectra of "as-received" CS (a) powder, 150 °C-heated CS (b), and 200 °C-heated CS (c).

vibration of C-O-C linkages in the glucosamine rings. From the representations of the secondary amide and methy groups, the "as-received" CS can be identified as partially N-acetylated chitosan,



where R is -COCH₃ and -H.

When the CS solution was heated at 150 °C, its spectral features (b) differed notably from that of the reference sample; the differences were as follows, (1) the development of three new bands at 1701, 1508, and 1402 cm⁻¹, (2) a shift of the NH₂-associated band at 1590 cm⁻¹ to a higher frequency side at 1619 cm⁻¹, (3) the disappearance of all the amide and methy group-related bands at 1654, 1549, 1419, 1372, and 1314 cm⁻¹. Regarding the result (1), the assignment of the new bands at 1701 cm⁻¹ is likely to be the C=O groups [5], and that at 1508 cm⁻¹ may be due to -NH₃⁺ Cl⁻, which is formed by the interaction between the pri-

mary amine and the HCL as the hydrolysis-promoter of CS [6]. A possible contributor of the new band at 1402 cm⁻¹ is the -NH₄⁺ band from the ammonium chloride salt, NH₄Cl [7]. Assuming that these assignments are valid, the result (3) gave us the following important information; the acetyl groups, CH₃OC-, seem to be removed from the partially N-acetylated CS by HCL-catalyzed hydrolysis, forming the acetic acid, CH₃COOH, and the -NH₃⁺ Cl⁻ complex derivatives. The latter derivative might be transformed into the NH₄Cl salt by further hydrolysis. As is seen in the spectrum (c), increasing the temperature to 200 °C led to the elimination of -NH₃⁺ Cl⁻-related band at 1508 cm⁻¹, a marked increase in intensity of the NH₄Cl absorption band at 1402 cm⁻¹, and an appreciable enhancement of C=O band at 1701 cm⁻¹, suggesting that the conformational transformation of -NH₃⁺ Cl⁻ into the NH₄Cl is promoted at elevated temperatures. Since such an HCL-induced deacetylation process introduces the formation of acetic acid derivative into the polymers, we assumed that the C=O band arose from the carboxylic acid groups, COOH, within the acetic acid molecule.

This information was supported by inspecting the XPS C_{1s} and N_{1s} core-level excitations for the 150- and 200 °C-heated film surfaces with CS/DEX ratio of 100/0. The films were deposited onto the Al substrate surfaces using the coating technology described earlier. In these core-level spectra, the scale of the binding energy (BE) was calibrated with the C_{1s} of the principal hydrocarbon-type carbon peak fixed at 285.0 eV as an internal reference standard. A curve deconvolution technique, using a DuPont curve resolver, was employed to substantiate the information on the carbon- and nitrogen-related chemical states from the spectra of the carbon and nitrogen atoms. In the C_{1s} region (Fig. 2), the 150 °C-heated bulk CS films had the four resolvable Gaussian components at the BE positions of 285.0, 286.5, 288.0, and 289.5 eV. The major peak at 285.0 eV is assignable to the C in CH_n groups as the principal component. According to the literature [8, 9], the second intense peak at 286.5 eV reflects both the C in -CH₂O- (e.g. hydroxide and ether) and in the C-N bond, and the contributor to the third intense peak at 288.0 eV is due to the C in C=O groups, while the weak signal, emerging at 289.5 eV, originates from C in the carboxylic acid, -COOH. In contrast, the spectral feature of the 200 °C-treated film was characterized by a conspicuous growth of the C=O and COOH carbon peaks. The N_{1s} spectrum (Fig. 2) of the 150 °C CS films included the major peak at 399.8 eV, revealing the N in primary amine [10], and the two shoulder peaks at 401.2 and 402.5 eV, belonging to the N originated from the amide groups [11] and ammonium ion-based salts [12]. By comparison, the curve structure of the 200 °C films was different from that of the 150 °C ones; in particular, there was (1) a striking decay of the amide N peak at 401.2 eV and (2) an increased intensity of the ammonium salt N signal at 402.5 eV. These data strongly supported the results from the FT-IR study; namely, the HCL-catalyzed hydrolysis, followed by heat treatment at 150 and 200 °C, introduces the acetic acid and ammonium chloride derivatives into the films. These

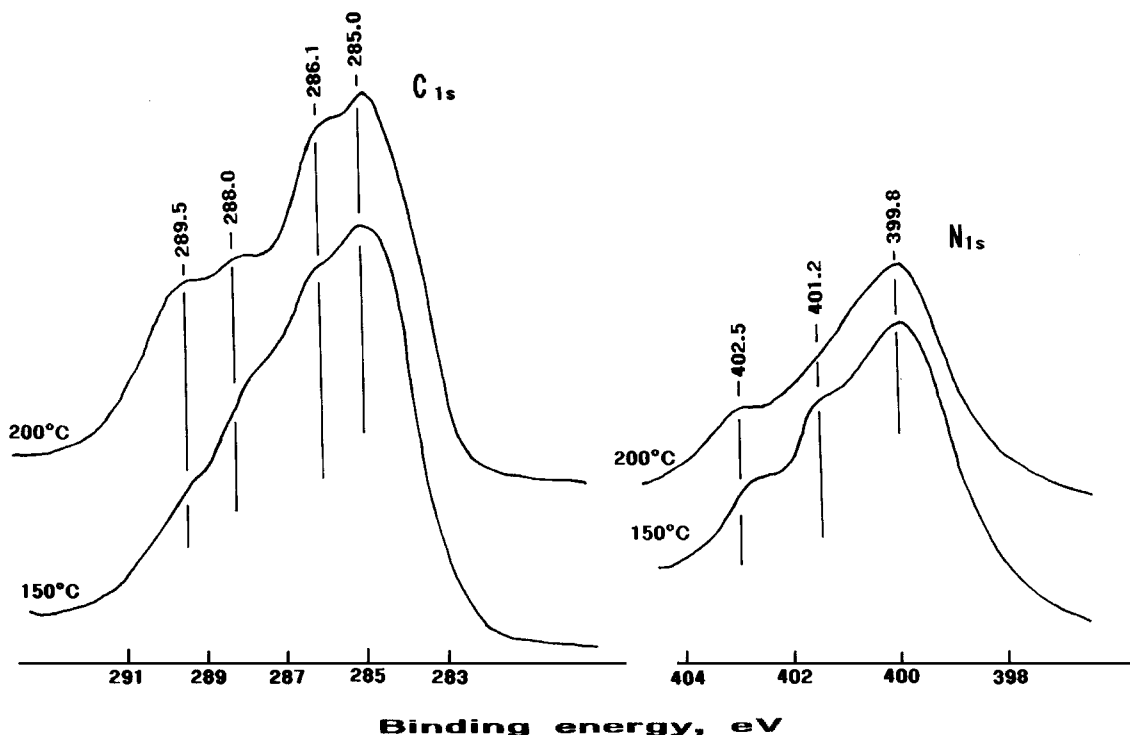
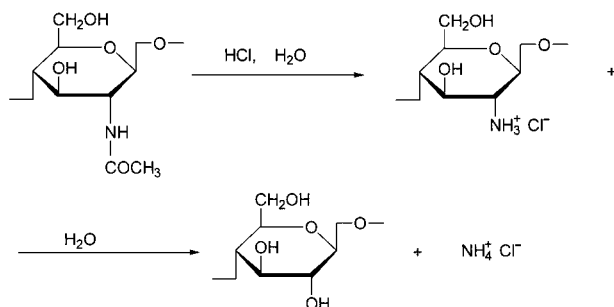
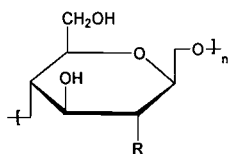


Figure 2 C_{1s} and N_{1s} core-level spectra for 150- and 200°C-treated CS film surfaces.

derivatives may be formed by the following hypothetical deacetylation pathways:



If such conformational changes take place, the molecular structure of the deacetylated CS can be illustrated as follows:



where R is NH_2 or OH. Based upon these information, our emphasis next centered on investigating the changes in the molecular conformation of the CS brought about by varying the CS/DEX ratio at 200°C. Fig. 3 shows the FT-IR spectra of CS/DEX samples with ratios of (a) 0/100, (b) 100/0, (c) 90/10, (d) 70/30, (e) 50/50, (f) 30/70, and (g) 10/90. As described in our previous papers [1], the Ce(VI) nitrate-oxidized bulk DEX (0/100 ratio), as the reference sample, indicated the formation of a Ce-complexed carboxy-

late, which could be defined from the two absorption bands at 1588 and 1407 cm^{-1} . Also, this spectrum had a strong peak at 1701 cm^{-1} due to the $C=O$ group in the carboxylic acid, and the four weak absorption bands at 1478, 1149, 1078, and 1026 cm^{-1} . The last three bands arose from the C-O-C linkage-associated groups, while the peak at 1478 cm^{-1} is ascribed to the methylene. This information suggested that Ce-linked carboxylate complexes, $-COO^- Ce^{4+} -OOC-$, were generated in three-step reaction schemes [13]. First, oxidation of the glycosidic rings initiated by the Ce ion generated aldehydic groups, $-HC=O$, after the opening of rings caused by cleavage of the C-C bonds in the glycol groups. Second, further oxidation of DEX led to the breakage of the C-O-C linkages in the opening structures of two oxidized compounds, the 3, 4-dihydroxybutanoic acid $[(HO)_2C_3H_5COOH]$ and glycolic acid $(HOCH_2COOH)$, as the fragmental products of glucose units. Once these oxidized fragments containing functional carboxylic acid groups were produced, in a final reaction step, these functional groups favorably reacted with Ce to form three Ce-bridged fragment complexes, $[(HO)_2C_3H_5COO^- Ce^{4+} -OOC_3(OH)_2] \cdot 2OH^-$, $(HOCH_2COO^- Ce^{4+} -OOC_2COH) \cdot 2OH^-$, and $[(HO)_2C_3H_5COO^- Ce^{4+} -OOC_2COH] \cdot 2OH^-$ [14]. The spectrum (b) represents the bulk CS sample (100/0 ratio) in which the contributors to these absorption bands were already described in the previous pages. When a 10 wt % by weight of the total amount of CS was replaced by DEX, the spectrum (c) exhibited the incorporation of two additional bands at 1655 and 1554 cm^{-1} into the bulk CS spectrum, revealing the formation of amide I and amide II, respectively. As seen in the spectrum (d) of the 70/30 ratio sample, further replacement of the CS by DEX resulted in the growth of these bands; meanwhile, the

peak intensities of NH_2 - and $-\text{NH}_4^+ \text{Cl}^-$ -related bands at 1620 and 1402 cm^{-1} had weakened. This interesting spectrum was also showed that there were no peaks at 1588 and 1407 cm^{-1} , originating from the formation of Ce-complexed carboxylate. A possible interpretation of these findings was that the NH_2 group in the CS has a strong chemical affinity for the Ce-bridge carboxylate complexes in the DEX, so forming the amide bond, $-\text{NHCO}-$, as the reaction product that grafts directly the fragmental products of DEX onto the CS. The hypothetical conformation of DEX fragment-grafted CS can be represented in three reaction schemes (Fig. 4). Returning to Fig. 3, the spectral feature (e) of the 50/50 ratio sample closely resembled that of the 70/30 ratio one. As expected, incorporating an excessive amount of DEX into the CS left unreacted Ce-complexed carboxylate fragments in the samples. In fact, the spectra (f) and (g) of the 30/70 and 10/90 ratio samples, respectively, included the two absorption bands at 1588

and 1407 cm^{-1} , belonging to the fragmental Ce-bridged carboxylate complexes; concurrently, a declining intensity of the amine-, amide- and NH_4Cl -related peaks at 1655, 1620, 1554, and 1402 cm^{-1} was observed. Thus, adding a proper amount of DEX to the CS seems to be necessary to avoid staying unreactive DEX fragments in the film.

One concern in applying natural polymer-based coating films as corrosion-preventing barriers to the metal surfaces was the fact that they absorb a large amount of atmospheric moisture. Such a hydrophilic property, which allows water to infiltrate the film easily, is one of the undesirable factors for use as the coating materials to mitigate corrosion of the metals. Hence, our attention was centered on the uptake of the moisture by the DEX-modified CS polymers. In this study, the 200°C -treated DEX-modified and unmodified CS powders were exposed for 10 hours in an environmental chamber under a 70% relative humidity (R.H.) at 25°C , and then they were examined by DSC to obtain the information on the extent of water uptake. As reported by Lelievre [15] and Donovan [16], the degree of the hydration for the polysaccharide could be determined from the DSC endothermic phase transitions, such as the enthalpy (ΔH) of dehydration occurring in the samples at temperature ranging from 25 to 200°C . Fig. 5 illustrates the DSC traces for the samples of (a) 100/0, (b) 90/10, (c) 70/30, (d) 50/50, (e) 30/70, (f) 10/90, and (g) 0/100 CS/DEX ratios after exposure in a 70% R.H. at 25°C . The DSC curve of the unmodified bulk CS sample (100/0 ratio) showed that the onset of endothermic transition begins at around 130°C , and ends near 250°C ; concurrently, the endothermic peak occurs at 165.3°C . From this information, we assumed that the dehydration of moisture-absorbed bulk CS was completed at temperature range of $130\text{--}250^\circ\text{C}$. When the CS was modified with DEX, a specific feature of the DSC curves was characterized by generating an additional endothermic peak at 134°C . The heat flow of this new exothermic peak seemed to increase with a decreasing ratio of CS to DEX, while heat flow at 165.3°C peak tends to decline. Furthermore, the curve (f) of the 10/90 ratio samples indicated an additional endothermic peak at 203.9°C . From the comparison with that of the bulk DEX (g), it is possible to rationalize that this new transition peak at 203.9°C was due to the thermal decomposition of unreacted DEX. Also, the curve of the bulk DEX had a dehydration-related peak at 110°C in the temperature range $60\text{--}190^\circ\text{C}$. If the postulated contributors to these exothermic transitions are valid, the peak at 134°C is more likely to be associated with the dehydration of DEX fragment-grafted CS reaction products rather than that of the DEX fragment itself.

To estimate the extent of absorption of the moisture, the enthalpy ΔH of dehydration occurring in the first endothermic phase transition was computed using the following formula [17, 18]: $\Delta H = T R A / h m$, where T , R , A , h , and m refer to the temperature scale ($^\circ\text{C in.}^{-1}$), the range sensitivity ($\text{mcal s}^{-1} \text{ in.}^{-1}$), the peak area (in.^2), the heating rate ($^\circ\text{C s}^{-1}$), and the sample weight (mg), respectively. The changes in ΔH as a function of the proportion of CS to DEX are given in Fig. 6. A

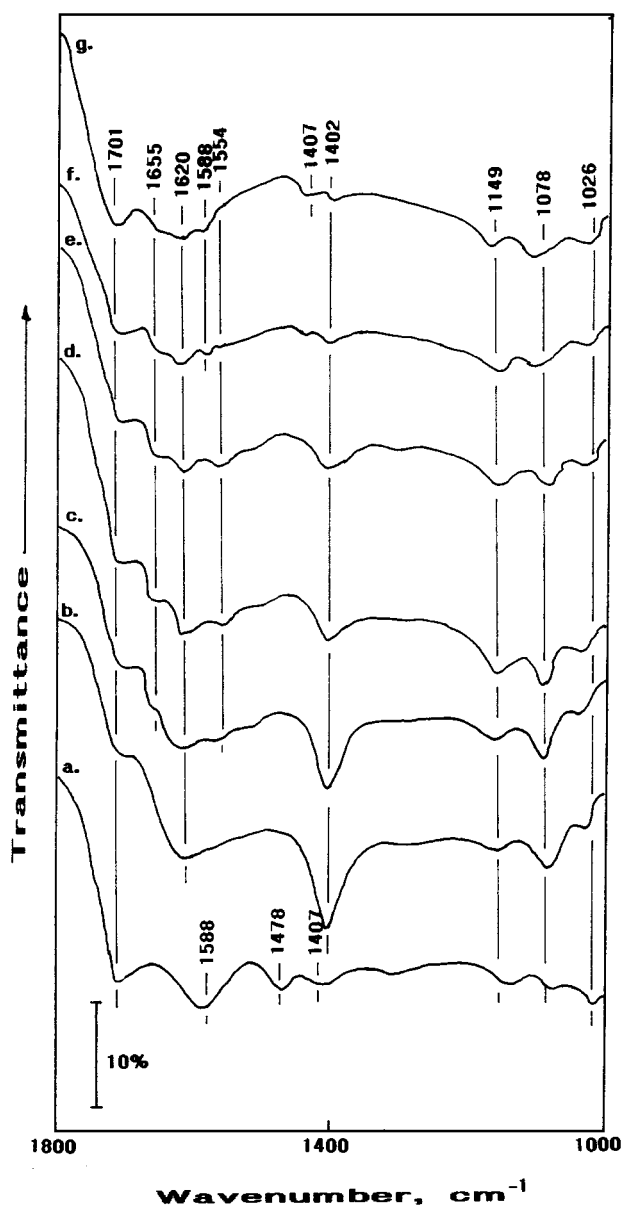


Figure 3 FT-IR spectra for the samples made with 100/0 (a), 90/10 (b), 70/30 (c), 50/50 (d), 30/70 (e), 10/90 (f), and 0/100 (g) CS/DEX ratio at 200°C .

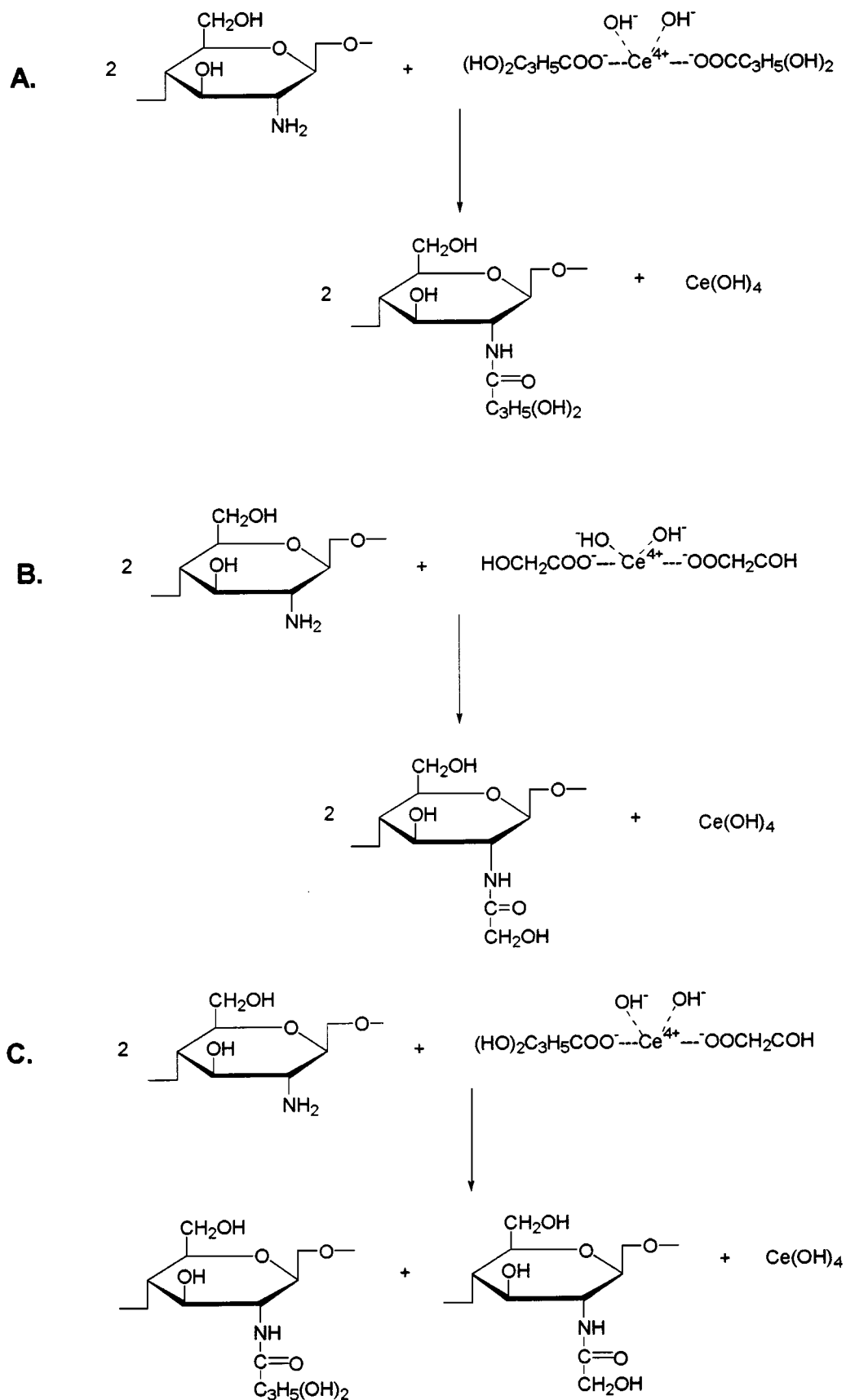


Figure 4 Hypothetical reaction schemes between D-glucosamine and Ce-bridged carboxylate complexes.

given result showed that the ΔH value was markedly reduced as the CS/DEX ratio declined from 100/0 to 70/30. The ΔH value of 0.084 kJ g^{-1} for the 70/30 ratio sample was three times lower than that of the bulk CS sample (100/0 ratio); beyond this, a further decrease

in the CS/DEX ratio caused an increase in ΔH value. Because the ΔH value reflects the total energy consumed for removing all the moisture adsorbed to the CS samples, we judged that the samples with a low value of ΔH are less susceptible to water uptake. From

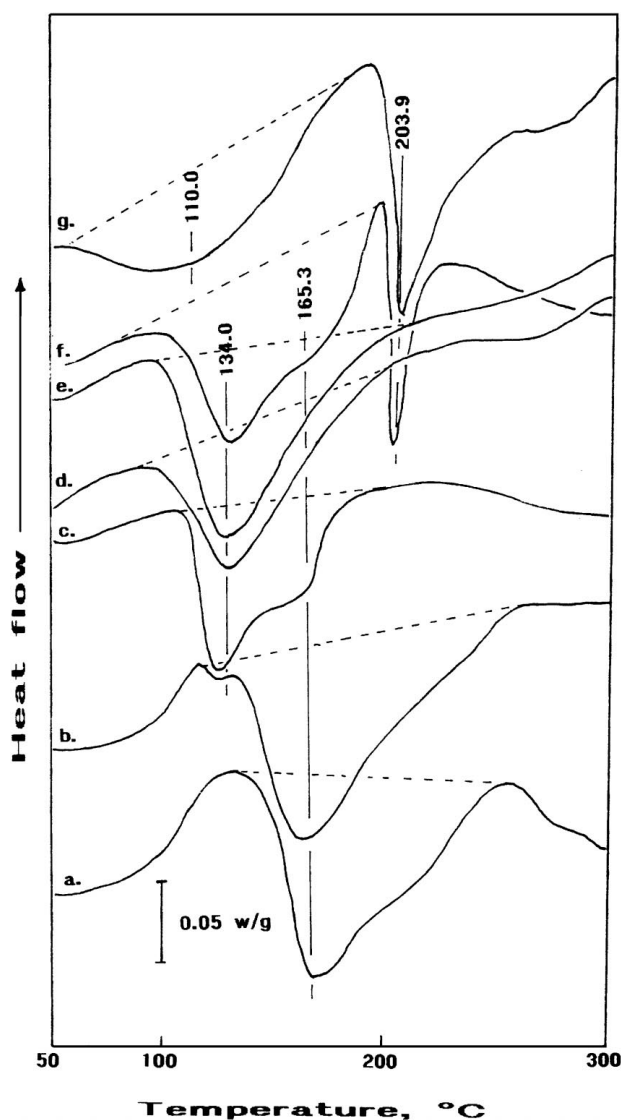


Figure 5 DSC endothermal curves for 100/0 (a), 90/10 (b), 70/30 (c), 50/50 (d), 30/70 (e), 10/90 (f), and 0/100 (g) ratio samples after exposure to a 70% R.H. at 25 °C.

this aspect, both the bulk CS and DEX samples with a very high ΔH of $> 0.16 \text{ kJ g}^{-1}$ appear to have a high susceptibility to the absorption of moisture. By comparison, the 70/30 and 50/50 ratio samples had an ΔH of less than 0.1 kJ g^{-1} , inferring that a proper proportion of CS to DEX plays an important role in reducing the magnitude of sensitivity to moisture. In other words, almost all the hydrophilic NH_2 groups present in the CS might react with all hydrophilic DEX fragments to yield the hydrophobic amide bonds as the reaction products, promoting the degree of fragment grafts on the CS. Therefore, there may be few, if any, remaining unreacted NH_2 groups and fragments in the grafted CS structure.

3.2. Characteristics of coatings

Based upon the information above, focus was now directed toward assessing the characteristics of the DEX fragment-grafted CS coating films deposited on the Al substrate surfaces. The characteristics to be assessed included the magnitude of wettability of the coating film surfaces by the water, the film-forming performance,

and the morphological feature and elemental compositions of their surfaces. All the data obtained were correlated directly with the results from the corrosion-related tests, such as electrochemical impedance spectroscopy (EIS) and salt-spray resistance.

One of the important factors indispensable for good protective coating films is the hydrophobic characteristic that the assembled film surfaces are not sensitive to moisture. To gain information on this characteristic, we measured the contact angle of a water droplet on the 200 °C-treated 100/0, 90/10, 70/30, 50/50, 30/70, 10/90, and 0/100 ratio film surfaces. If the contact angle was low, we concluded that the film is sensitive to moisture. A high degree of sensitiveness may allow the water to permeate through the film easily, and, in the worst case, it may promote the hydrolysis-induced decomposition of the film. A plot of the average value of the advancing contact angle, θ (deg.), as a function of CS/DEX ratios is shown in Fig. 7. The resultant θ -ratio data exhibited that the θ value of bulk CS film (100/0 ratio) considerably increases as it was modified with the DEX, especially in the CS/DEX ratio range of 100/0 to 70/30. The 70/30 ratio coating film had the highest θ value of 60°, corresponding to a 2.9 times greater than that of the bulk CS. A further incorporation of EDX into the CS caused a declining θ value, strongly suggesting that the film with a lower sensitivity to moisture could be made by incorporating a proper amount of DEX into the CS. Thus, this finding can be taken as evidence that an increase in the degree of grafting serves in providing a less sensitive film surface to moisture. In the other words, the hydrophilic characteristics of the individual CS and DEX fragment coatings are converted into hydrophobic ones by the grafting reaction between them, inferring that the DEX fragment-grafted CS coating films made of a suitable proportion of CS to DEX will contain a minimal amount of hydrophilic unreacted fragments and D-glucosamine components. The major factor governing this conversion is the formation of amide bonds yielded by the grafting reaction, conferring a less wettability of water over the film surfaces. Also, this information substantially supported our earlier results on the uptake of the moisture by the DEX-modified CS polymers.

Attention was next paid to exploring the surface morphology and microtexture of coating films covering Al surfaces, by SEM. In this experiment, three coating films made with 100/0, 70/30, and 10/90 ratios were deposited on Al at 200 °C. The data obtained would provide information on the film-forming performance of grafted and non-grafted CS polymer coatings. The SEM image of the brown-colored 100/0 ratio film (Fig. 8A) revealed a discontinuous microtexture containing numerous microcracks, allowing the corrosive solutions to permeate through the film layer easily. Such development of cracks in the film may be due to a high degree of shrinkage of the film encountered during drying at 200 °C, and also to the conformational changes in CS structure caused by the deacetylating reaction that introduces the formation of CH_3COOH and NH_4Cl derivatives in it. In contrast, an excellent film-forming performance was observed from the 70/30

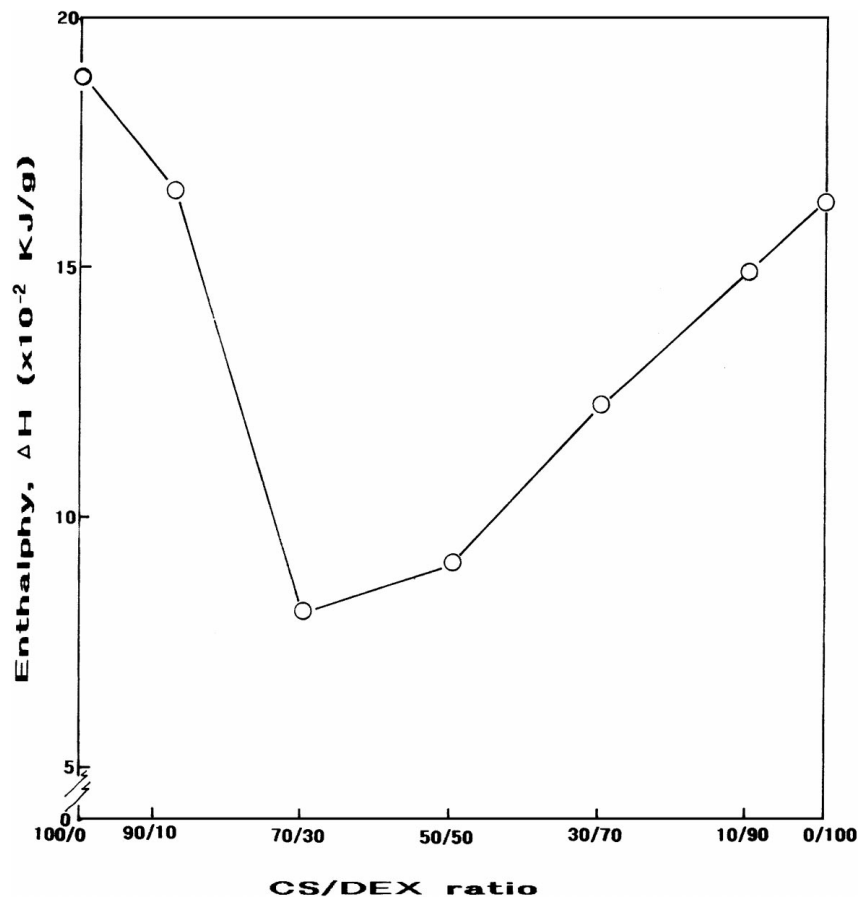


Figure 6 Changes in enthalpy which represent the magnitude of dehydration as a function of CS/DEX ratio.

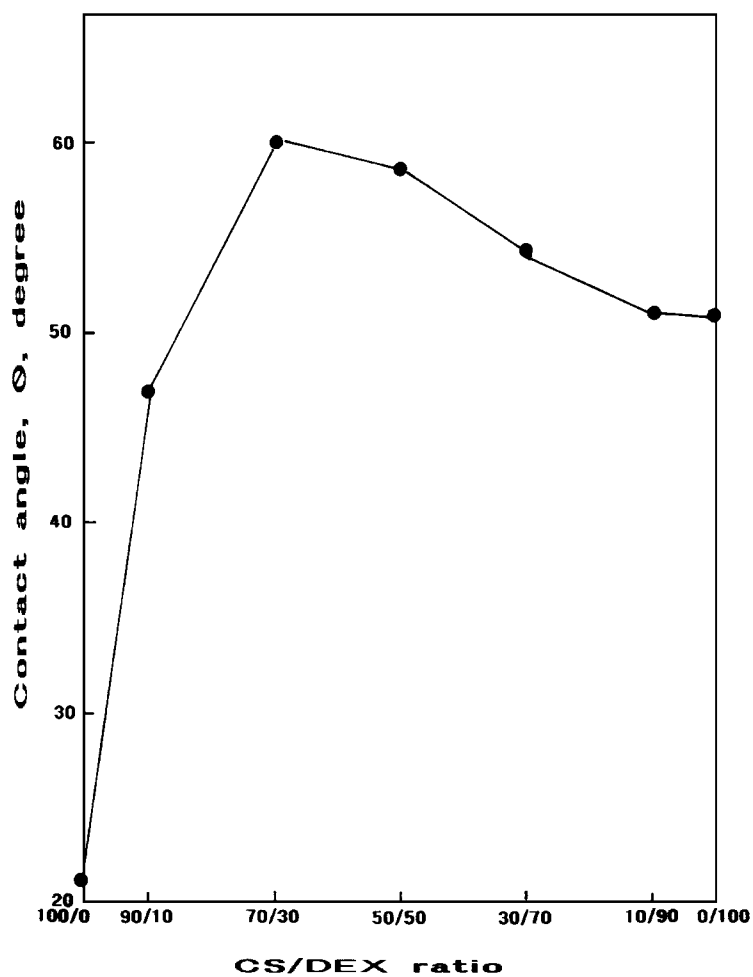


Figure 7 Contact angle of a water droplet on 200 °C-treated coating film surfaces with various different CS/DEX ratios.

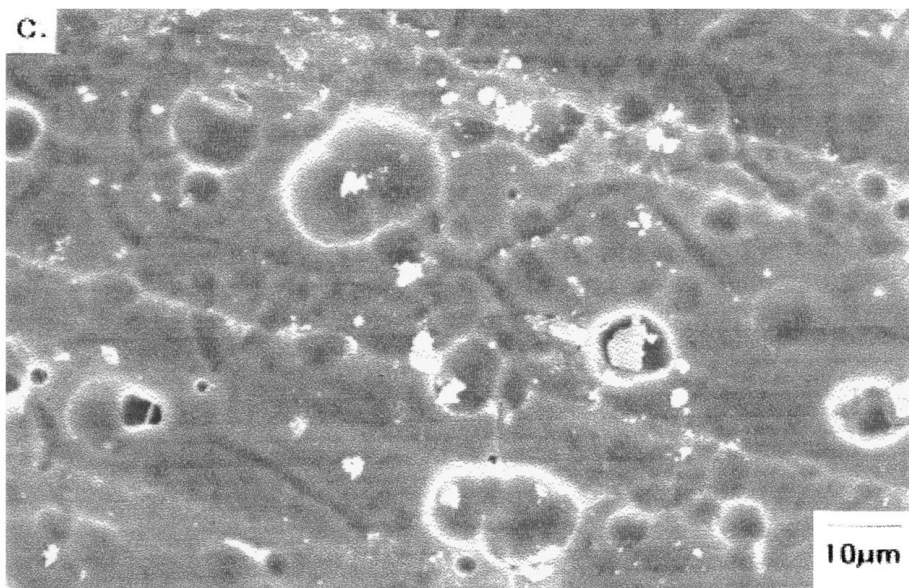
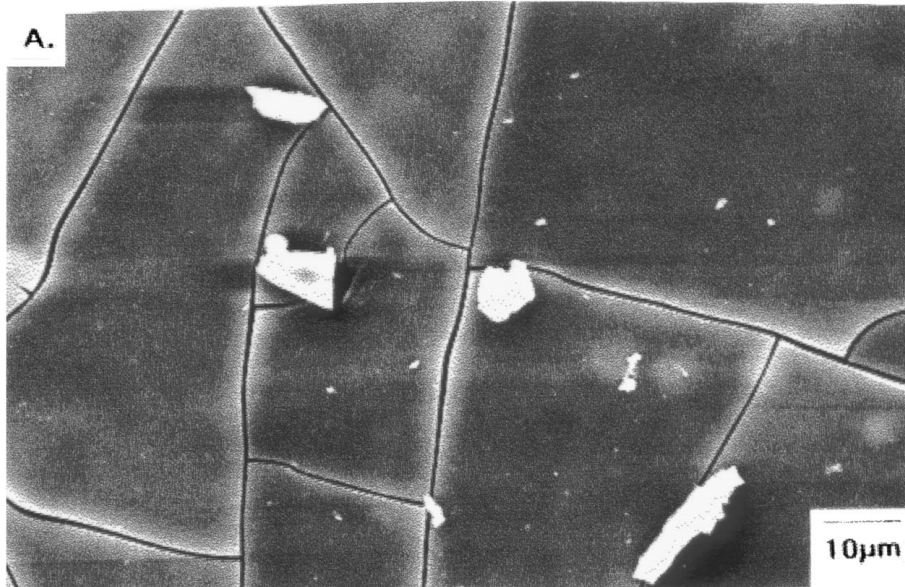


Figure 8 SEM images of 200 °C-treated 100/0 (A), 70/30 (B), and 10/90 (C) CS/DEX ratio coating films.

ratio-derived coatings, which were light brown in color (Fig. 8B); SEM disclosed a continuous, uniform film with a smooth surface morphology, seemingly suggesting that grafting the DEX fragments onto the CS serves in reducing the development of shrinkage-related stress cracks in the CS itself. There is no doubt that lack of defects and blemishes is one of the most important factors in ensuring that the coatings adequately protect the metals against corrosion. Increasing the amount of DEX in the blended systems led to the changes in color of films from brown to light yellow. With the 10/90 ratio, the SEM image (Fig. 8C) shows a continuous film covering the Al surfaces. Furthermore, the disclosure of a rough underlying Al surface signifies that a thin transparent film was formed.

All the data were integrated and correlated directly with the effectiveness of grafted CS films in protecting the Al substrates from corrosion. Using a surface-profile measuring system, the thickness of the 100/0, 90/10, 70/30, 50/50, 30/70, and 0/100 CS/EDX ratio films was ~ 3.2 , ~ 2.8 , ~ 2.4 , ~ 1.9 , ~ 1.6 , and ~ 0.9 μm , respectively. Although intuitively a thicker coating film may be expected to have a better corrosion-protective performance than a thin one, AC electrochemical impedance spectroscopy (EIS) was used to evaluate their effectiveness as corrosion-preventing barriers. On the overall Bode-plot curves [the absolute value of impedance $|Z|$ ($\Omega\text{ cm}^2$) vs. Frequency (Hz)], (not shown), our particular attention was paid to the impedance value in terms of the pore resistance, R_p , which can be determined from the plateau in the Bode plot occurring at a sufficiently low frequency of 5×10^{-2} Hz. Fig. 9 shows the plots of R_p of 200 °C-treated coating films versus the CS/DEX ratios. The R_p value (not shown) of the uncoated Al substrate was $\sim 5.0 \times 10^3 \Omega\text{ cm}^2$. When the Al surfaces were coated with the single CS and DEX coatings, or DEX-modified CS coatings, the R_p value increased by one or two orders of magnitude over that of the substrate. The R_p

value of the single CS coatings with the thickest film of $\sim 3.2 \mu\text{m}$ was $\sim 1.7 \times 10^4 \Omega\text{ cm}^2$. When a 10% of the total amount of CS was replaced by DEX, this value was an order of magnitude greater than that of the unmodified CS. With further substitution, the value of R_p increased: the 70/30 ratio coatings had the highest R_p of $4.0 \times 10^5 \Omega\text{ cm}^2$. However, coatings made by incorporating an excessive amount of DEX into the CS showed a decreasing R_p value. In fact, the R_p value of the 50/50 ratio coating declined $\sim 55\%$ to $1.8 \times 10^5 \Omega\text{ cm}^2$, compared with that of the 70/30 ratio. In the 10/90 ratio coating, the R_p value fell further to $1 \times 10^5 \Omega\text{ cm}^2$. As expected, the bulk DEX coating had a lower R_p value of $3.5 \times 10^4 \Omega\text{ cm}^2$, corresponding to an order of magnitude lower than that of the 70/30 ratio coating. Since the R_p value reflects the magnitude of ionic conductivity generated by the electrolyte passing through the coating layers, a high R_p value means a low degree of permeation of electrolyte into the coating films. Thus, the DEX fragment-grafted CS polymer conformation offers improved performance in minimizing the rate of permeation of the electrolytes through the coating layers, compared with those of the individual CS and DEX coatings. Hence, we believed that a grafted structure would lead to a low uptake of electrolytes by the coatings. The data also represented that the changes in the magnitude of conductivity depend on the CS/DEX ratio. Comparing R_p values, the effectiveness of these ratios in ensuring a low degree of infiltration of electrolyte was in the following order; 70/30 > 50/50 > 90/10 > 30/70 > 10/90 > 0/100 > 100/0. The most effective coating system in reducing the permeability of electrolytes was the 70/30 ratio with a $4.0 \times 10^5 \Omega\text{ cm}^2$.

Fig. 10 represents the changes in R_p at 5×10^{-2} Hz for the 200 °C-treated coating specimens as a function of exposure times of up to 20 days in a 0.5 N NaCl solution at room temperature. In the first five days of exposure, three coating systems, 90/10, 70/30, and 50/50 ratios, showed no changes in R_p value, compared with that of the unexposed ones. Afterwards, their R_p values gradually fell with an increasing exposure time. In contrast, the rate of uptake for all the other coating systems was much higher than that of these three coatings; in fact, a marked decrease in R_p can be seen after exposing them for 5 days. When the R_p value dropped to a less than $5 \times 10^3 \Omega\text{ cm}^2$, no further exposure test was made because the R_p at this level is mainly due to the anodic etching of the underlying Al. In fact, the pitting corrosion of Al caused by the failure of the coating was visually observed in these specimens. The data also indicated that the 70/30 and 50/50 ratio coatings after a 20-day exposure still maintained an $R_p > 10^4 \Omega\text{ cm}^2$. Implicating this finding with the data on FT-IR, XPS, DSC, and contact angle, two factors played an essential role in conferring resistance to metal corrosion: First was the polymer conformation containing amide bonds formed by the grafting reaction between Ce-complexed carboxylate in DEX fragments and NH_2 groups in CS; and second was the lesser susceptibility of the coating surfaces to moisture due to the enhanced degree of grafting, together with a minimal amount of hydrophilic unreacted fragments and CS.

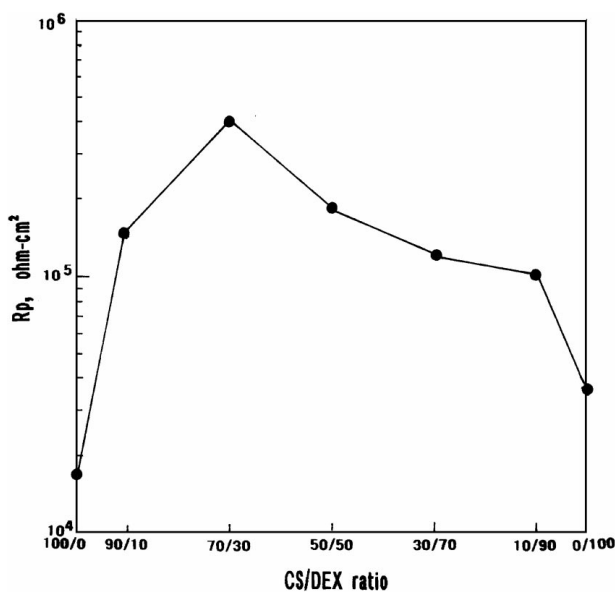


Figure 9 Pore resistance, R_p , value of Al panel samples coated with 100/0, 90/10, 70/30, 50/50, 30/70, 10/90, and 0/100 CS/DEX ratios at 200 °C.

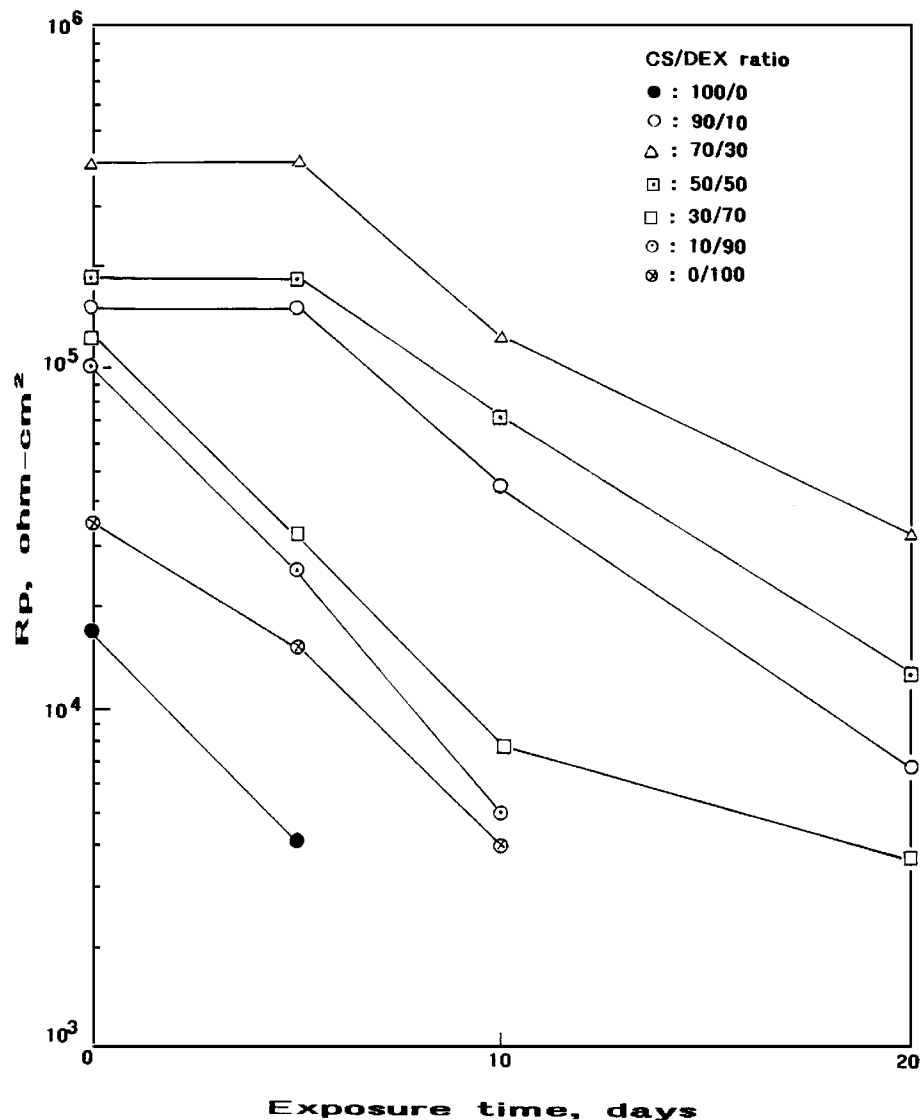


Figure 10 Change in R_p for 100/0, 90/10, 70/30, 50/50, 30/70, 10/90, and 0/100 ratio-coated Al as a function of exposures up to 20 days.

This information on the EIS was supported by salt-spray resistance tests for the coated panels treated at 200 °C (Table I). A trace of rust stain was generally looked for in evaluating the results for salt-sprayed panel specimens. The results were reported as the total exposure time at the date of the generation of the rust stain from the Al surfaces. As is seen, the entire surfaces for the single CS (100/0 ratio)- and DEX (0/100 ratio)-coated Al panels were corroded after exposure to the salt spray for 72 hours, corresponding to only 24 hours longer than that of the uncoated bare Al (not shown), suggesting that the ability of these coatings

to protect Al against corrosion is poor. By comparison with these single coatings, the DEX fragment-grafted CS coating systems displayed a far better performance in reducing the rate of corrosion. With the 90/10 ratio, the resistance to salt spray extended seven times to 504 hours. A further improvement in conferring resistance was observed from the coatings containing increased concentrations of DEX, signifying that an increase in the grafting of DEX fragment onto the CS imparts improved resistance to corrosion. In fact, coatings, made from 70/30 ratio served in providing a great protection of Al against corrosion for 720 hours. However, a further incorporation of DEX into the CS caused a declining resistance to salt spray.

TABLE I Salt-spray resistance tests for DEX fragment-grafted CS coatings

CS/DEX ratio	Salt-spray resistance, hours
100/0	72
90/10	504
70/30	720
50/50	590
30/70	216
10/90	120
0/100	72

4. Conclusion

In approaching ways of using partially N-acetylated chitosan (CS) marine polymer ground from the crab or shrimp shells in a water-based coating system to protect aluminum (Al) substrates against corrosion, we modified it with natural dextrine (DEX) polymers derived from corn starch. Both are renewable resources and environmentally benign. The DEX-modified CS

paints as film-forming precursor solutions were prepared by incorporating a DEX aqueous solution containing Ce nitrate hexahydrate as the oxidizing agent into CS aqueous solution containing HCL as the hydrolyzing agent. The blended two polysaccharide polymer solutions were deposited onto the Al surfaces using a simple dip-withdrawing coating method and converted into the thin solid films by heating them at 200 °C in air. The oxidation of DEX led to the formation of two oxidized compounds, 3,4-dihydroxybutanoic acid and glycolic acid, as the fragmental products. These fragments next favorably reacted with Ce from the Ce nitrate to reconstitute Ce-complexed carboxylate fragmental compounds. Adding HCL to the CS solution not only enhances its solubility in water, but also served to remove acetyl groups from the CS. The primary amine, NH₂, in the deacetylated CS, had a strong chemical affinity for the Ce-bridged carboxylate fragments to create secondary amide linkages that serve in grafting the DEX fragments onto the CS. An increase in the degree of grafting resulted in the formation of an uniform, continuous, defect-free coating films that offer a less susceptible to moisture and a low permeation of electrolyte species through the coating layers, conferring a good protection of metal against corrosion. However, incorporating an excessive amount of DEX into the CS generated undesirable coating films with a high degree of wettability of surfaces and an enhanced magnitude of ionic conductivity caused by electrolytes passing through the coating layers. These negative factors could be accounted for by the persistence of a certain amount of unreacted hydrophilic fragments in the coatings. Nevertheless, the most effective coating film for mitigating the corrosion of Al was derived from precursor solution with CS/DEX ratio of 70/30. This coating film deposited onto the Al surfaces offered a lesser sensitivity to moisture, and improved pore resistance (in $\Omega \text{ cm}^2$) by an order of magnitude higher than those of the single CS and DEX coatings, and conferred salt-spray resistance for 720 hours.

Acknowledgement

This work was performed under the auspices of the U.S. Department of Energy, Washington, D.C. under Contract No. DE-ACO2-98CH10886, and supported by the U.S. Army Research Office Program MIPR 96-40.

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Received 23 October

and accepted 18 November 1998