Interfacial Properties of Chitosan and Nonylphenol Polyoxyethylene Ether

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Received 10 September 2008; accepted 11 October 2009
DOI 10.1002/app.31646
Published online 14 January 2010 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Nonylphenols are water-soluble surfactants that are used extensively in industry and are found in many consumer products. Nonylphenol polyoxyethylene ether (known commercially as TX-100), which is one of the most popular members of this family, has a detrimental effect on the environment. Adding chitosan to a solution of TX-100 reduces the amount of surfactant required while maintaining its surface activity. We evaluated the interfacial properties, including the surface tension, contact angle, and particle size, as well as the fluorescence and Fourier transform infrared spectra of various test solutions prepared from three stock solutions: (1) chitosan dissolved in dilute acetic acid, (2) TX-100 dissolved in deionized water, and (3) a mixed chitosan/TX-100 solution. Previous results revealed that low concentrations of TX-100 are relatively harmless to the environment; in this study, we found that its surface activity at a higher concentration was equal to that of its chemical mixture with chitosan. In addition, we found that the presence of chitosan improved the stability of emulsions of TX-100. The micellar particles were small, and the stability of the emulsion was maximized at a TX-100 to chitosan ratio of 7 : 3. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 116: 2227–2233, 2010

Key words: fluorescence; FT-IR; interfaces; surfactants

INTRODUCTION

Nonylphenol is used primarily to produce nonylphenol polyethoxylates (NPnEOs). Although the release of nonylphenol itself into the environment is forbidden, aerobic or anaerobic microbes can lead to the release of toxic metabolized products of NPnEOs into the environment.[1] During this decomposition process, the number of hydrophilic ethylene oxide (EO) units is gradually reduced; when the decomposed nonylphenol derivative contains no or very few EO groups, its water solubility is poor, and this causes nonylphenol to accumulate in the environment. Furthermore, because microbes cannot decompose nonylphenol, environmental pollution persists.[2] Figure 1 depicts the structures of several nonylphenol derivatives: NPnEOs, nonylphenol polyethoxy carboxylic acids, and oxide-metabolized carboxylate nonylphenol polyethoxy carboxylic acids. These chemicals, which are not decomposed readily in the environment, are typically called *persistent nonylphenolic compounds*.[3,4]

Nonylphenols are generally good surfactants that are used extensively in industry and are found in many consumer products. In the environment, these surfactants can decompose into nonylphenol itself; although it is not very toxic, the structure of nonylphenol is similar to that of estrogen (Fig. 2). Nonylphenol acts as an environmental hormone that interferes with the regulation of glandular excretion and might destroy the procreative capacity of some animals.[5–7]

Chitosan, a (1→4)-linked 2-amino-2-deoxy-β-D-glucan, is completely or partially derived from deacetylated chitin.[8] Chitin is a cationic biopolymer found in the shells of shrimp, crabs, and insects. Chitosan generally retains its bioactivity after chemical treatment and is very compatible with biomes. Because of its unique nutritional and physiochemical properties, chitosan is applied extensively in the food, cosmetic, textile, and pharmaceutical industries and in wastewater treatment.[9–13] Many of these applications involve the interactions between chitosan and anionic surface-active materials, such as phospholipids, small-molecule surfactants, or bile acids. The effective application of chitosan in the food industry depends on an understanding of the origin and nature of these interactions.[14–16]

The interactions between chitosan and surfactants in aqueous solutions have been studied extensively to obtain a fundamental understanding of the process and to determine potential applications.[17–19] In aqueous solutions, chitosan undergoes complicated aggregation behavior in the presence of typical anionic surfactants; thus, it has become the subject of

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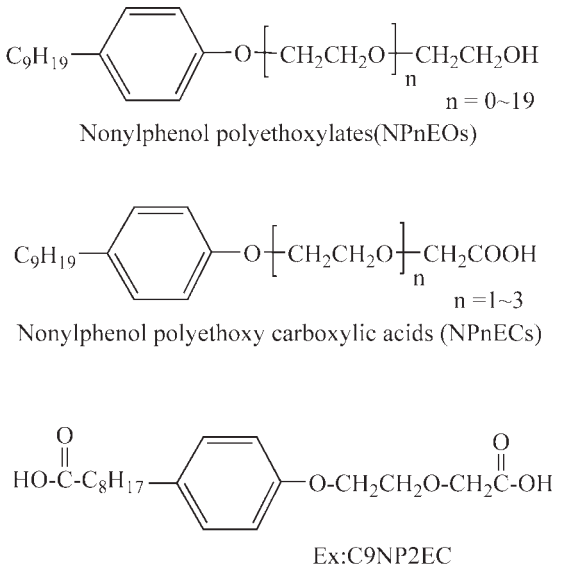


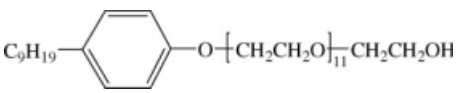
Figure 1 Chemical structures of nonylphenol-based surfactants and pollutants.

various scientific and technological investigations.[20,21] Adding surfactants to solutions containing hydrophobically associated polymers drastically affects their structural, dynamic, and rheological features.[22–24] In this study, we investigated the changes in the surface tension, wettability, surface activity, and emulsion stability that occurred after the addition of chitosan to solutions of nonylphenol polyoxyethylene ether (known commercially as TX-100). We also studied the molecular interactions that occur between chitosan and TX-100 upon mixing.

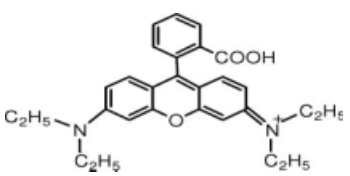
EXPERIMENTAL

Chemicals

1. Chitosan (weight-average molecular weight = 58,000) was purchased from Sheen-Yee Chemical Co. (Taiwan); its structure is displayed in Figure 3.
2. TX-100 was purchased from Sino-Japan Chemical Co. (Japan):



3. The fluorescence agent rhodamine B was purchased from Koch-Light Chemical Co. (St. Louis, MO):



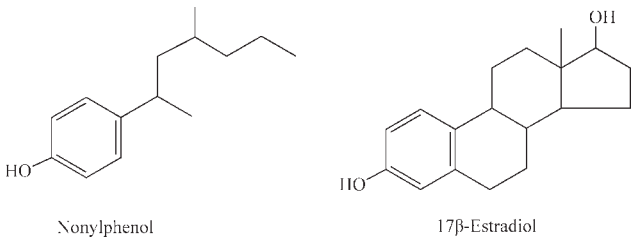


Figure 2 Chemical structures of nonylphenol and estradiol.

Preparation of the stock solutions

1. Preparation of the stock solution of chitosan: 1 g of chitosan was dissolved in 100 g of 2% (w/w) diluted acetic acid.
2. Preparation of the stock solution of TX-100: 1 g of TX-100 was dissolved in 100 g of deionized water.
3. Preparation of the stock solution of TX-100 and chitosan: solutions 1 and 2 were combined in weight ratios of 3 : 7, 1 : 1, and 7 : 3 and mixed thoroughly.

Measurement of the surface tensions

Three of the stock solutions—chitosan, TX-100, and their 1 : 1 mixture—were diluted to prepare solutions featuring another 11 concentrations of each (0.2, 0.15, 0.1, 0.05, 0.01, 0.005, 0.0025, 0.0005, 0.0001, 0.00005, and 0.00001 wt %). The surface tension of each solution was measured separately at room temperature with a CBVP-A3 surface tensiometer (Japan Kaimenkaguka), which was calibrated with ultrapure water before use. The platinum plate was cleaned through flaming; the glassware was rinsed sequentially with tap water and ultrapure water. The surfactant solution was prepared afresh as a stock solution and then diluted to the concentration desired for each measurement. The surface tension was measured three times at each concentration; the average error was less than 0.5 dyn/cm.

Measurement of the contact angles

Three of the stock solutions—chitosan, TX-100, and their 1 : 1 mixture—were diluted to prepare another seven test solutions of each (0, 0.1, 0.2, 0.5, 1.0, 1.5, and 2.0 wt %). The contact angle of each solution was

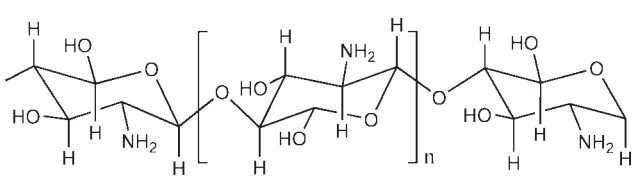


Figure 3 Chemical structure of chitosan.

measured separately with a FACE CA-5 contact-angle meter (USA). An acrylic plastic sheet was used.

Measurement of the fluorescence spectra

1. An aqueous solution of dilute rhodamine B (30 ppm) was prepared in the dark.
2. Separately, 0.5-g aliquots of the water blank, chitosan stock, and TX-100 stock solutions and the three combined stock solutions (3 : 7, 1 : 1, and 7 : 3) were taken; to each sample, 49.5 g of diluted rhodamine B was added, and it was mixed thoroughly. Each spectrum was recorded separately.

The emission spectra of the solutions were measured with an Aminco-Bowman series 2 luminescence spectrometer (Brookfield, WI). The excitation wavelength was 350 nm; the emission was measured between 370 and 800 nm.

Particle size analysis

1. The stock solutions of chitosan and TX-100 and the three combined stock solutions (3 : 7, 1 : 1, and 7 : 3) were diluted to form 1 wt % aqueous solutions (100 g).
2. Ten grams of each of these samples was decanted; next, 10 g of olive oil was added to each solution. Each sample was thoroughly mixed in a rotating mixer operated at 11,000 rpm for 5 min to obtain a good emulsion. The particle size of each sample was measured.

A Microtrac model S3000 particle sizer (Montgomeryville, PA) was used to measure the average particle diameters and the distributions of the surfactants under dynamic circulation.

Measurement of the Fourier transform infrared (FTIR) spectra

FTIR spectra were recorded directly from the stock solutions of chitosan, TX-100, and their 1 : 1 mixture. IR spectra were recorded in the range of 4000–650 cm^{-1} with a PerkinElmer Spectroscopic FT/IR-3 spectrophotometer (Waltham, MA); the compound was spread on the KBr disk. For each sample, 32 scans were collected with a resolution of 4 cm^{-1}.

Measurement of the chemical oxygen demand (COD)

COD tests were performed with Merck COD reagents (Whitehouse Station, NJ) and a HACH spectrophotometer (Loveland, CO).

RESULTS AND DISCUSSION

Surface tension

Molecules in a liquid are generally stressed uniformly in all directions, so the resulting force is zero.

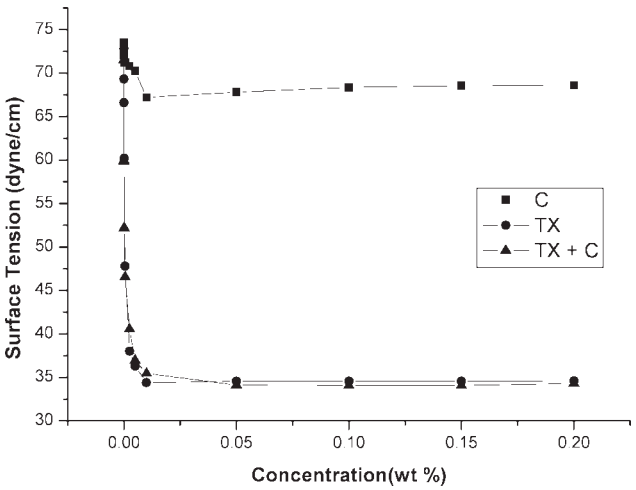


Figure 4 Surface tensions of three stock solutions with respect to their concentrations: chitosan (C), TX-100 (TX), and their 1 : 1 mixture.

When the liquid molecules are located at the surface, however, they will experience different forces from the air and from the liquid. Theoretically, this phenomenon is negligible. Unequal intermolecular forces at the surface of a liquid are responsible for surface tension because the molecules on the surface are pulled inward whereas those in the bulk are pulled equally in all directions by adjacent liquid molecules. The surface tension of pure water is 72.4 dyn/cm at 25°C; when a surfactant is present, however, it drops to a value that depends on the volume added.

Figure 4 displays plots of the surface tension of the chitosan, TX-100, and combined TX-100/chitosan (1 : 1) stock solutions. Chitosan itself did not exhibit any surface activity; the surface tension of its solutions remained in the range of 65–70 dyn/cm. The structure of TX-100 comprises terminal hydrophilic and hydrophobic functional groups; therefore, it has a dramatically low critical micelle concentration of 0.005–0.01 wt %. Hence, the surface tension of its solutions decreased significantly to less than 35 dyn/cm. The combined TX-100/chitosan (1 : 1) stock solution exhibited a positive active surface effect. When the concentration of this combined stock solution was 0.05 wt %, its surfactancy was better than that of TX-100. Hence, the addition of chitosan to TX-100 maintained its surface activation while reducing the amount of surfactant required, and this suggested that this process would contribute substantially to environmental protection.

Contact angles

Most surfactants reduce the surface tension and surface energy of liquids while increasing their diffusion, penetration, and wettability. *Wettability* generally refers to the adsorbability of a gas or

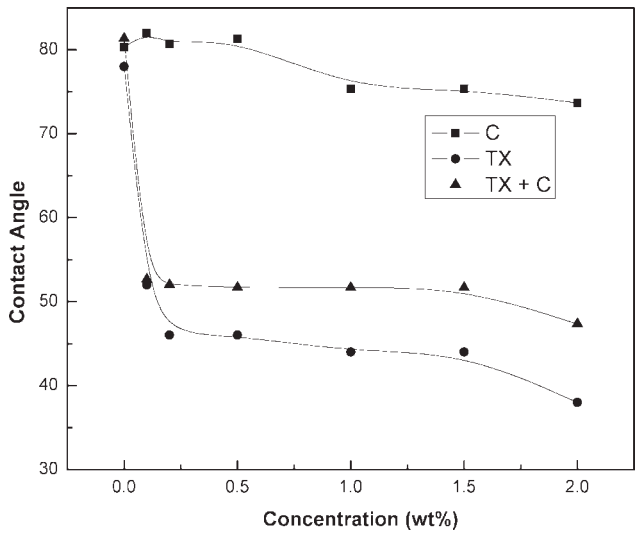


Figure 5 Contact angles of three stock solutions with respect to their concentrations: chitosan (C), TX-100 (TX), and their 1 : 1 mixture.

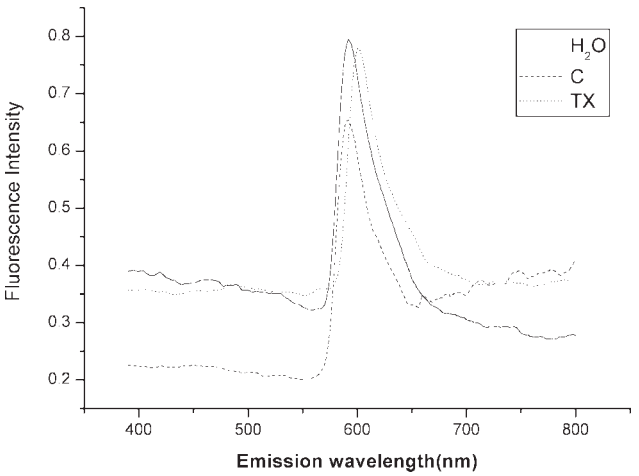


Figure 6 Fluorescence intensities and emission wavelengths of rhodamine B solutions in water and in aqueous solutions of chitosan (C) and TX-100 (TX).

liquid at the surface of a solid when the various phases come into contact. The wettability of a liquid can be determined from the contact angle of a drop of liquid placed onto a solid surface. A smaller contact angle generally corresponds to greater wettability.

Figure 5 displays the contact angles of the stock solutions of chitosan, TX-100, and their 1 : 1 mixture at various concentrations. Because chitosan has some of the properties of a biopolymer but not of a surfactant, its pure solutions exhibited contact angles that did not change obviously, and they remained at about 75°. In contrast, TX-100 behaves as a surfactant; when its concentration was increased up to 0.2 wt %, its contact angle decreased significantly from 78 to 46°. This decline was less dramatic when we increased the concentration beyond this point. Because the combined TX-100/chitosan stock solutions featured mutual interactions between their components, their contact angles remained within certain ranges depending on the ratio of TX-100 to chitosan. When the concentration of the combined solution (1 : 1) increased from 0 to 0.2 wt %, the contact angle decreased markedly from 81 to 52°; when the concentration exceeded 1.5 wt %, the angle declined again. Generally, the contact angle of the combined stock solution remained at about 50°. According to these contact-angle tests, chitosan itself exhibited only a slight degree of wettability, but this wettability was improved by the addition of TX-100 to chitosan in a 1 : 1 ratio without the surface activation of TX-100 changing.

Fluorescence spectra

When an atom or molecule is excited ($S_0 \rightarrow S_n$) by absorbing a photon, it may release some of its energy ($S_1 \rightarrow S_0$) by emitting through internal conversion and instantaneous vibrational relaxation. This emission of light fluorescence has a very short attenuation time of 10^{-9} to 10^{-7} s. The use of luminescence probes is predicated upon certain molecules displaying a selective affinity for a unique site in an aggregate; the nature of the probe environment is reflected in the emission properties.[25] We evaluated the microenvironment of chitosan and TX-100 surfactants by considering the emission spectra of rhodamine B. The end of a long hydrophobic hydrocarbon chain tends to aggregate into dimers in an aqueous solution. Furthermore, the dimer favors dissociation to the end of the monomer at the critical micelle concentration of the surfactant. These phenomena can indicate the polarity of the microenvironment in which the rhodamine B molecules are present (e.g., micelles).[26]

The fluorescent intensities of rhodamine B in water, chitosan, and TX-100 follow the order of water > TX-100 > chitosan (Fig. 6). Because it has the weakest fluorescence intensity, chitosan exhibits the lowest surface activation with respect to those of TX-100 and water.

The fluorescence intensities of rhodamine B in the three combined stock solutions of TX-100 and chitosan followed the order of 3 : 7 < 1 : 1 < 7 : 3 (Fig. 7); that is, the intensity of the fluorescence of the combined stock solution increased with the concentration of TX-100 increasing because TX-100 has a lower critical micelle concentration than chitosan. The fluorescent intensity is directly proportional to the surface activation.

Comparing the maximum fluorescence intensities of rhodamine B in water and in the three combined stock solutions (Fig. 8), we found that a higher content of chitosan affected the surfactancy of the

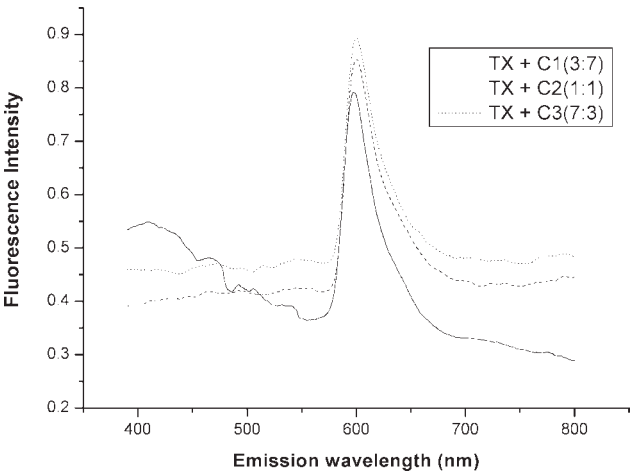


Figure 7 Fluorescence intensities and emission wavelengths of rhodamine B in stock solutions of three different TX-100 (TX) and chitosan (C) mixtures (3 : 7, 1 : 1, and 7 : 3).

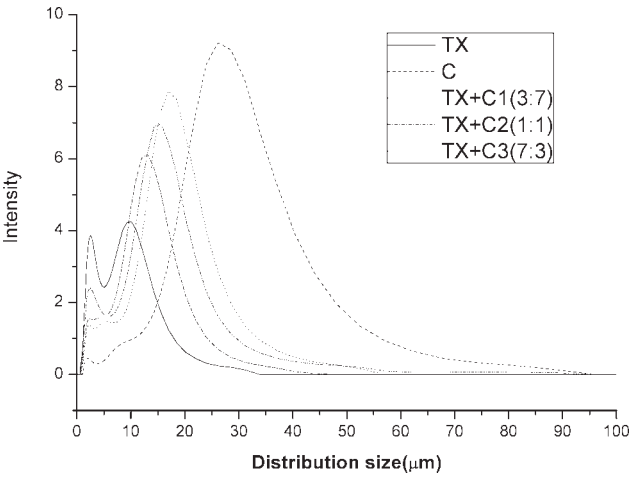


Figure 9 Particle size analyses of stock solutions of TX-100 (TX), chitosan (C), and three mixtures (3 : 7, 1 : 1, and 7 : 3).

solution detrimentally. Chitosan had the poorest surfactancy; the 7 : 3 stock solution of TX-100 and chitosan had the greatest.

Particle size

The particle size and homogeneity of an emulsion are critical to its stability. The distribution of particle sizes is one of the most important factors determining the quality of an emulsion. In particle size analysis, a wider or greater number of peaks suggests a lower sample stability. Figure 9 reveals that the particle size distribution of chitosan was very wide and that it had the greatest mean particle size (30 μm). As a result, chitosan exhibited the poorest emulsification. In contrast, TX-100 is a nonionic surfactant with a narrow particle size distribution (mean particle size = 15 μm). Nevertheless, the particle size analysis of TX-100 yielded two peaks, and this suggested that its stability was not as high as would be expected, even though it could form a stable emulsion. When we added TX-100 to chitosan to form a combined stock solution, the curve in Figure 9 shifted toward smaller particles as more TX-100 was added. When the ratio of the two components was 1 : 1, the curve exhibited the narrowest features, and the corresponding particle size was the smallest (12 μm). When the ratio of the two was 7 : 3, the mixture possessed the optimal stability and ability to form an emulsion.

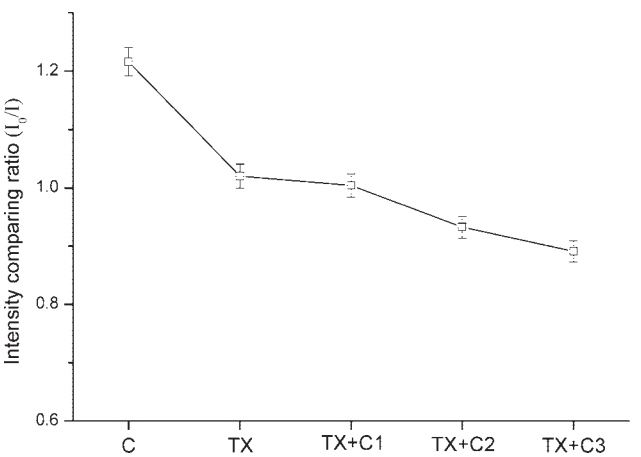


Figure 8 Maximum fluorescence intensities of rhodamine B in water (I_0) and in aqueous solutions containing chitosan (C), TX-100 (TX), and three mixtures (3 : 7, 1 : 1, and 7 : 3) (I).

FTIR spectra

When TX-100 and chitosan are combined in a particular ratio, the hydrophilic properties of chitosan are magnified and its interfacial activation is improved according to the analysis of fluorescence spectra. In fact, adding chitosan did not reduce the original surface activation properties of TX-100. The particle size measurements revealed that this combined stock solution formed a very stable emulsion, the particle distribution of which was very uniform. These new findings suggest that TX-100/chitosan mixtures have great potential for future applicability.

FTIR spectra can reveal interactions between molecules. Figure 10 displays the FTIR spectra of the stock solutions of TX-100, chitosan, and their 1 : 1 mixture. Table I presents the peak frequencies of the characteristic FTIR spectroscopic absorptions. The absorption peaks associated with the O—H and N—H stretching vibrations of TX-100, chitosan, and their 1 : 1 mixture are present in the range of 3200–3600 cm^{-1}. Comparing the signal of the OH functional groups in the combined stock solution with that of the chitosan-only solution, we observed a peak shift toward a higher wave number

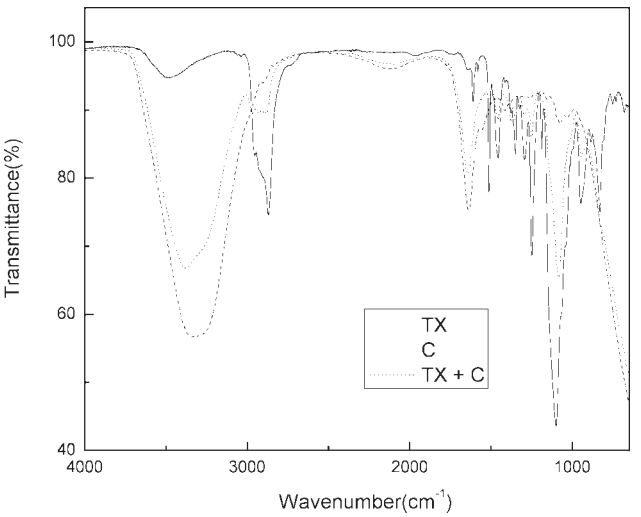


Figure 10 FTIR spectra of stock solutions of TX-100 (TX), chitosan (C), and their 1 : 1 mixture.

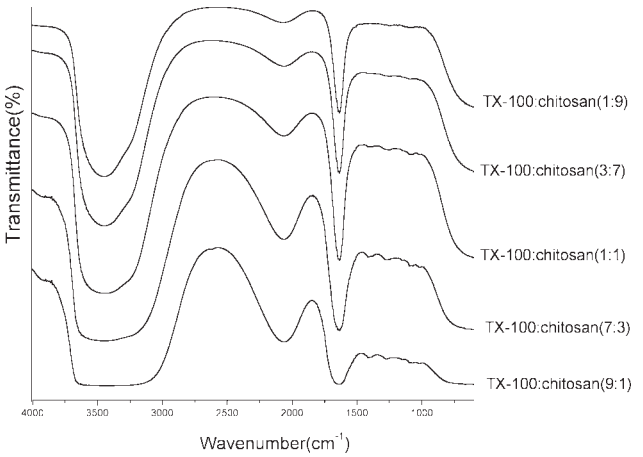


Figure 11 FTIR spectra of stock solutions of TX-100 and chitosan mixtures.

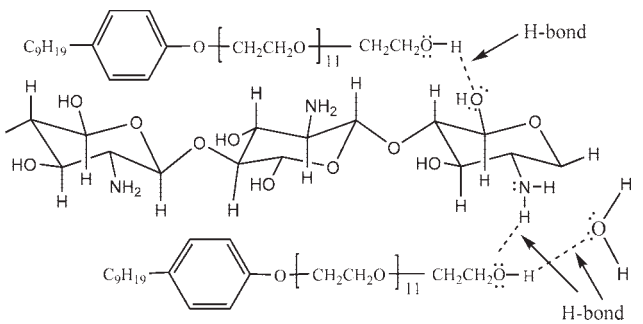
(3344 → 3381 cm^{-1}). Furthermore, the height of the peak from the combined stock solution differed from that from TX-100. Accordingly, we suspect that hydrogen bonds formed between the OH functional groups of chitosan and TX-100.

Comparing the signal of the characteristic absorption of the NH units in the combined stock solution with that of the chitosan-only solution revealed a shift to a higher frequency (1637→1643 cm^{-1}). The signal at 1609 cm^{-1}, associated with the C=C units in the benzene groups of TX-100, was also much lower in intensity. These results confirm that an intermolecular interaction occurred between the N—H functional groups of chitosan and the OH functional groups of TX-100.

For further explanation, it was observed from FTIR spectra in Figure 11 that as the proportion of chitosan and TX-100 changes, the absorptions also change drastically in the range of 3000–3600 cm^{-1}. This range includes the absorption peaks of N—H and O—H. Because the absorption peaks of the combined stock solutions are broader than those of chitosan and TX-100 in the range of 3000–3600 cm^{-1}, we infer that intermolecular interactions occur between N—H and O—H functional groups, as shown in Scheme 1. A new absorption peak also appears. Overall, as the absorption peak becomes broader, we infer that hydrogen bonds are produced between N—H from chitosan and O—H from TX-100 and water, and this also results in the shift of the absorption peak and the change of the absorption pattern. Altogether, the hydrogen bonding that occurs between TX-100 and chitosan explains the good interfacial activation and favorable stability of their various emulsions.

COD

After their use, surfactants (e.g., household detergents, personal care products, washing agents, and processing materials used in industry) are generally passed quantitatively into wastewater. Therefore, the constant input of surfactants into the environment requires that this class of compounds be subjected to thorough ecological characterization. Figure 12 presents the CODs of TX-100 and chitosan prepared in this study; lower COD corresponds to a lower



Scheme 1 Hydrogen-bonding interactions between chitosan, TX-100, and water.

TABLE I
Characteristic Absorptions (cm^{-1}) of Stock Solutions of Chitosan, TX-100, and Their 1 : 1 Mixture in FTIR Spectra

Sample	O—H	N—H (stretching)	C—H (stretching)	N—H (bending)	C=C (benzene)	C—O
Chitosan	3344	3242	2903	1637	—	1075
TX-100	3482	—	2871	—	1609, 1511	1100
TX-100 + chitosan	3381	3257	2879	1643	—, 1511	1084

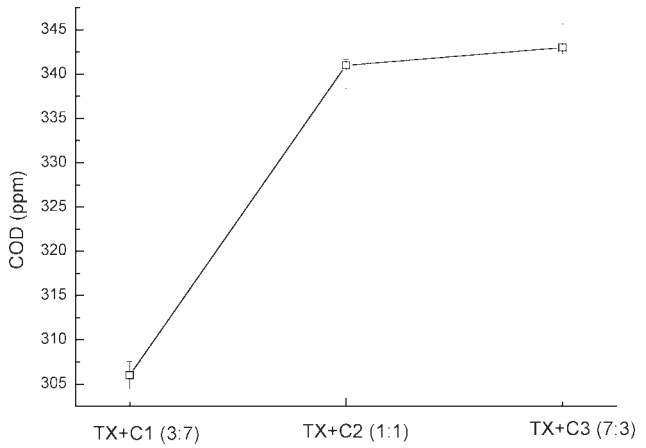


Figure 12 COD of stock solutions of TX-100 (TX) and chitosan (C) mixtures (3 : 7, 1 : 1, and 7 : 3).

impact on the environment. Our results suggest that mixing chitosan with TX-100 (3 : 7) can reduce the degree of environmental pollution.

CONCLUSIONS

Although it possesses good surfactancy and low toxicity, nonylphenol does not biodegrade readily, and this can result in environmental pollution. Nonylphenol also interferes with the secretion of hormones by animals, including humans, and thereby causes impotence. Chitosan is a biopolymer that exhibits several favorable properties, including high biodegradability, biological compatibility, biological activity, and nontoxicity. We have found that chitosan can be added to TX-100 to mitigate its negative effects. Surface tension and particle size analyses indicated that TX-100 exhibits excellent stability and emulsification when combined with chitosan in a ratio of 7 : 3; this combination also features the smallest micelle particles and a uniform particle distribution. Although a TX-100 to chitosan ratio of 1 : 1 provided good wettability, the surface activation was maximized when the ratio was 7 : 3. FTIR spectroscopy indicated the existence of intermolecular hydrogen bonds between the TX-100 and chitosan units, with the mixed solutions exhibiting very strong interfacial activation and forming stable emulsions only at particular ratios. Above all, our investigation reveals that the addition of chitosan reduces the quantity of TX-100 required in its role as a surfactant while maintaining its surface activation, reducing its surface tension, and optimizing its wettability; as a result, this approach may reduce the environmental impact of nonylphenol.

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