Immobilization of Chitosan on Nylon 6,6 and PET Granules Through Hydrolysis Pretreatment

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ABSTRACT: Chitosan has been increasingly studied as an adsorbent for removing heavy metal ions and organic compounds from aqueous solutions. Most of the studies used chitosan in the form of flakes, powder, or hydrogel beads. This research investigates the immobilization of chitosan on other granular materials to overcome the poor mechanical property of chitosan and offers the potential for chitosan to be used as a regenerable adsorbent. Nylon 6,6 and poly(ethylene terephthalate) (PET) granules were partially hydrolyzed under an acidic or alkaline condition to allow chitosan to be coated or immobilized on the granules' surfaces. The surface morphologies of nylon 6,6 or PET granules before and after hydrolysis and those with immobilized chitosan layer were examined by scanning electron microscopy (SEM), and their surface properties were characterized through ζ-potential analysis and X-ray photoelectron spectroscopy. The immobilization of chitosan on nylon 6,6 or PET granules was identified to be through the formation of the salt structure ($-NH_3^+ \cdots {}^-OOC-$) between the surfaces of hydrolyzed nylon 6,6 or PET granules and the chitosan layer. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 3973–3979, 2003

Key words: coatings; nylon; poly(ethylene terephthalate) (PET); hydrolysis; morphology

INTRODUCTION

Chitosan is a polycationic polymer derived from chitin, a major component of arthropods, and is readily available from seafood processing wastes.[1] Because chitosan has unique physiological and biological properties, it has been widely used as a versatile starting material for the preparation of various products in biomedical engineering.[2,3] In recent years, chitosan has also increasingly been studied as an adsorbent for the removal of heavy metal ions and organic pollutants from aqueous solutions because the amino and hydroxy groups on the chitosan chain can act as chelation or reaction sites for the substances to be removed.[4–7] Most of these adsorption studies used chitosan in the form of flakes, powder, or hydrogel beads. Hydrogel beads provided the potential advantage of regenerating or reusing the adsorbent. Because chitosan hydrogels contain a large amount of water in their network structure, they show poor mechanical properties that limit their actual applications. Although crosslinking of chitosan with glutaraldehyde (GLA),[8] epichlorohydrine (ECH),[9] tripolyphosphate (TPP),[10] or ethylene glycol diglycidyl ether (EGDE)[11] may enhance the strength of chitosan hydrogels,

crosslinking has been found to largely reduce the adsorption capacity of chitosan.[12,13] In addition, the crosslinking agents such as GLA and EGDE are not preferred because of their physiological toxicity. A recent study by Ji and Bai[14] reported the preparation of chitosan–poly(vinyl alcohol) (PVA) hydrogels for lead ion adsorption. The blending of chitosan with PVA was found to increase the strength of the chitosan hydrogels, attributed to the interactions between chitosan and PVA in the blend through hydrophobic side-chain aggregation and intermolecular and intramolecular hydrogen bonds. However, a more practical solution to the poor mechanical properties of chitosan is perhaps to coat or immobilize chitosan on other supporting materials. Nylon and poly(ethylene terephthalate) (PET) are two of the candidate matrices because they are inexpensive, inert, nontoxic, and readily available. The main drawback of PET as the supporting material is its high hydrophobicity, low wettability, and poor adhesion of the surface,[15] which makes coating or immobilization of chitosan difficult. Although nylon contains amino terminal groups, it is still classified as a hydrophobic polymer in many applications.[16] Plasma treatment is often an effective surface modification technique to improve wettability, bondability, and interaction ability of polymer surfaces. This process, however, is usually limited by equipment restrictions to smaller components and parts,[17] and is expensive.

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Chemical pretreatment can be another effective approach to improve surface conditions. Andrews et al.[18,19] used partial acid hydrolysis in the immobilization of enzymes and affinity ligands to thin nylon film. Ito et al.[20] studied immobilization of proteins on PET membrane by treating the membrane surface under an alkaline condition. In this research, we used partial acid hydrolysis for pretreatment of nylon 6,6 granules and partial basic hydrolysis for PET granules. Then, chitosan was coated or immobilized on the surface of the hydrolyzed granules through reactions between the amino groups of chitosan and the carboxyl groups of the granules. Characterization of the granules was carried out through scanning electron microscopy (SEM), zeta-potential measurement, and X-ray photoelectron spectroscopy (XPS).

EXPERIMENTAL

Materials

Chitosan was purchased from Sigma Chemical Co. (St. Louis, MO). Nylon 6,6 granules (diameter 3.0 mm; density 1.12 g/cm^3) were obtained from Solutia Inc. (St. Louis, MO). PET granules (diameter 3.0 mm; density 1.3–1.4 g/cm^3) were provided by Goodfellow Corp. (Cambridge, UK). Before use in the study, nylon 6,6 and PET granules were thoroughly washed with deionized (DI) water followed with methanol, and then dried under reduced pressure. All other chemicals used for the investigations were of analytical grade and DI water was used to prepare all the solutions.

Chitosan immobilization

Nylon 6,6 granules were placed in HCl solution (3.0M) with stirring for 2 h at 40°C for hydrolysis. PET granules were immersed in NaOH solution (4.0M) with stirring for 1 h at 45°C for hydrolysis, and then immersed in a dilute HCl solution (0.05M) at room temperature overnight for acidification. The hydrolyzed nylon 6,6 and PET granules were washed with DI water until the pH value of the washing liquid became the same as that of the fresh DI water, and then the granules were stored in DI water before use for chitosan immobilization.

The chitosan solution for coating or immobilization was prepared by dispersing a 4 g amount of chitosan flakes in 200 mL of 2% (v/v) acetic acid solution and was stirred for 4 h at 60°C. The hydrolyzed nylon 6,6 or PET granules were then taken from the stock and immersed in the chitosan solution with stirring for 1 h at room temperature, followed by soaking in NaOH solution (2.0M) for another 12 h. Finally, the granules were separated from the solution and washed with

cold and hot DI water to a pH about 6, then dried at 40°C for 48 h before surface analysis.

XPS analysis

XPS was used to determine the surface composition and the chemical environment of the granules. The XPS measurements were made on a VG ESCALAB MKII spectrometer (Manchester, UK) with an Al–K$_\alpha$ X-ray source (1486.6 eV photons). The analyzer pass energy was 80 eV. The granules were mounted on the standard sample studs by means of double-sided adhesive tape. The core-level signals were obtained at a photoelectron take-off angle of 75° (with respect to the sample surface). The X-ray source was run at a reduced power of 150 W (15 kV and 10 mA). The pressure in the analysis chamber was maintained at 7.5 × 10^{-9} Torr or lower during each measurement. All binding energies (BEs) were referenced to the C1s hydrocarbon peak at 284.6 eV. In peak fit, the linewidth [full width at half maximum (FWHM)] of the Gaussian peaks was maintained constant for all components in a particular spectrum. Surface elemental stoichiometries were determined from peak/area ratios, after correcting with the experimentally determined sensitivity factors, and were reliable to ±5%.
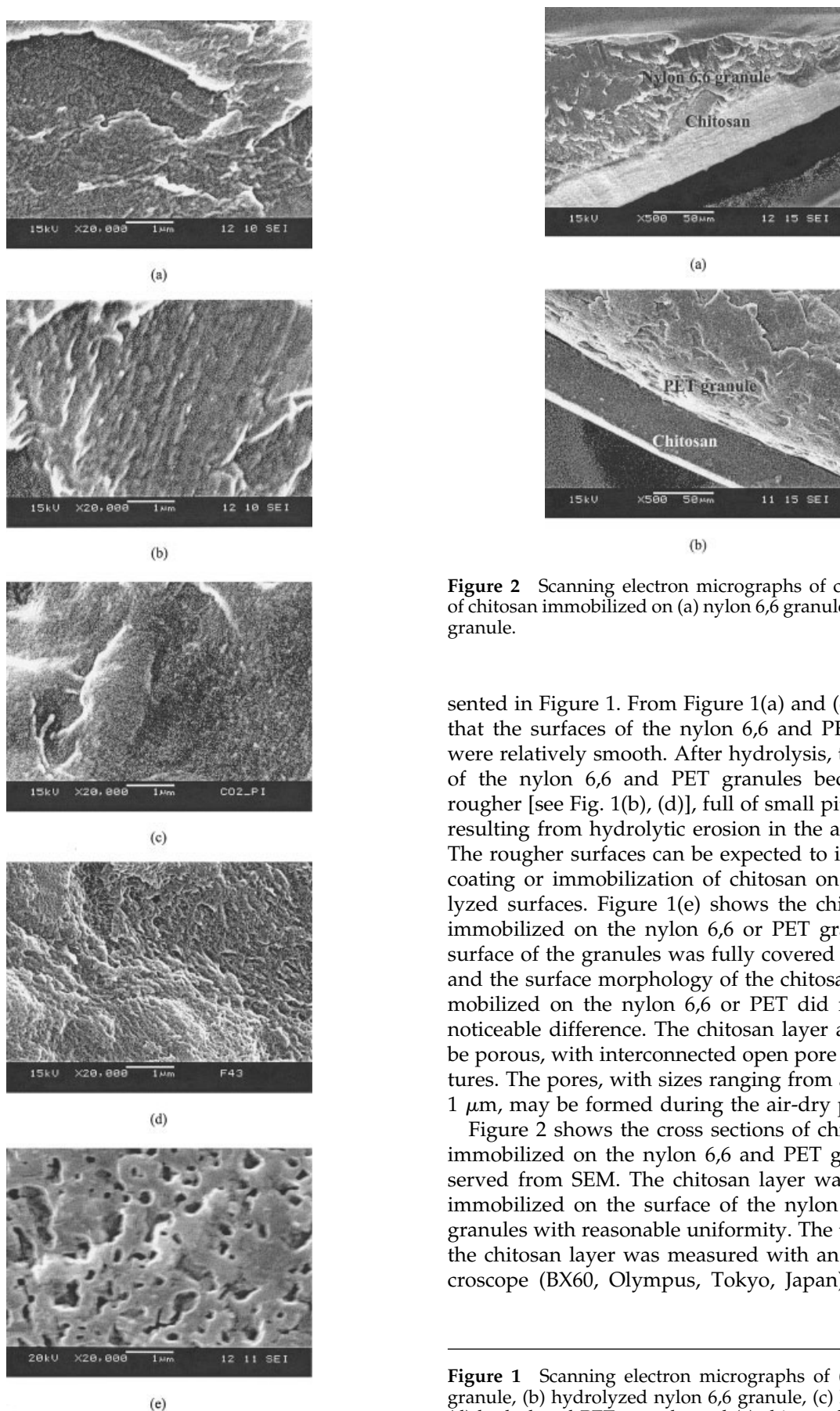
SEM and ζ-potential studies

The surface morphologies of the granules were examined using a scanning electron microscope (SEM, JSM-6400; JEOL, Peabody, MA) involving bombardment of the surface with an electron beam emitted from a tungsten wire at 15–20 kV. The granules were mounted on a metal sample substrate by double-sided adhesive tape, and the surface was coated with platinum powder before scanning with the microscope.

A Zeta Plus4 Instrument (Brookhaven Instruments Corp., Holtsville, NY) was used to determine the surface ζ-potentials of the granules by the method described by Bai and Tien.[21] The granules were placed in a 100-mL vial with 50 mL DI water and the vial was vibrated in a sonic bath for 30 min. The liquid in the vial with small fragments from the surface was then decanted for measurements, and the ζ-potential so determined was assumed to be that of the surface. The pH of the samples was adjusted with HCl and NaOH solutions as necessary.

RESULTS AND DISCUSSION

Surface morphologies

SEM micrographs showing the surface morphologies of the nylon 6,6 and PET granules before and after the hydrolysis reaction and the granules with coated or immobilized chitosan layer on the surface are pre-

(a)

(b)

(c)

(d)

(e)

Figure 1 Scanning electron micrographs of (a) nylon 6,6 granule, (b) hydrolyzed nylon 6,6 granule, (c) PET granule, (d) hydrolyzed PET granule, and (e) chitosan layer.
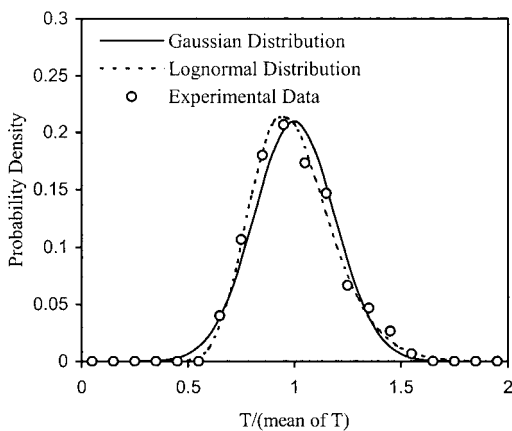

(a)

(b)

Figure 2 Scanning electron micrographs of cross sections of chitosan immobilized on (a) nylon 6,6 granule and (b) PET granule.
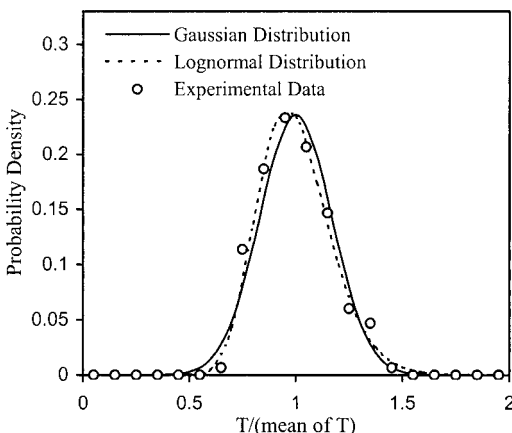
sented in Figure 1. From Figure 1(a) and (c), it is seen that the surfaces of the nylon 6,6 and PET granules were relatively smooth. After hydrolysis, the surfaces of the nylon 6,6 and PET granules became much rougher [see Fig. 1(b), (d)], full of small pits or craters resulting from hydrolytic erosion in the acid or base. The rougher surfaces can be expected to improve the coating or immobilization of chitosan on the hydrolyzed surfaces. Figure 1(e) shows the chitosan layer immobilized on the nylon 6,6 or PET granules. The surface of the granules was fully covered by chitosan and the surface morphology of the chitosan layer immobilized on the nylon 6,6 or PET did not show a noticeable difference. The chitosan layer appeared to be porous, with interconnected open pore microstructures. The pores, with sizes ranging from about 0.1 to 1 μm, may be formed during the air-dry process.

Figure 2 shows the cross sections of chitosan layer immobilized on the nylon 6,6 and PET granules observed from SEM. The chitosan layer was coated or immobilized on the surface of the nylon 6,6 or PET granules with reasonable uniformity. The thickness of the chitosan layer was measured with an optical microscope (BX60, Olympus, Tokyo, Japan), equipped

(a) nylon 6,6 granules

(b) PET granules

Figure 3 Measured experimental thickness data fitted to Gaussian and lognormal distribution.

with the software AnalySIS®3.0 (Soft Imaging System GmbH; Asia Headquarter, Cyberjaya, Malaysia), for 50 individual chitosan-immobilized granules at three different cutting edges per granule. The 150 data of the measured chitosan layer thickness were fitted to a Gaussian or lognormal distribution function $f(x)$, where $x = T/\overline{T}$, and T represents the thickness of the chitosan layer and $\overline{T}$ represents the mean of the thickness, with definitions as follows:

Gaussian distribution

$$f(x) = \frac{\exp[-(x - \bar{x})^2/2\sigma^2]}{\sqrt{2\pi}\sigma} \tag{1}$$

where $\bar{x}$ is the mean of x and σ is the standard deviation of x.

Lognormal distribution

$$f(x) = \frac{\exp[-(\ln x - \overline{\ln x})^2/2\sigma_1^2]}{\sqrt{2\pi}\sigma_1 x} \tag{2}$$

where $\overline{\ln x}$ is the mean of $\ln x$ and σ_1 is the standard deviation of $\ln x$.

The calculation gave the mean ($\overline{T}$) of the thickness of the chitosan layer immobilized on the nylon 6,6 granules and PET granules as 42.36 and 48.97 μm, respectively. Figure 3 shows the fit of the Gaussian distribution and the lognormal distribution (expressed in terms of the standard distribution) to the measured experimental thickness data. The critical values χ^2 for the Gaussian distribution based on a statistical chi-squared test, which compares the experimental and predicted values, are 0.2 for both the nylon 6,6 and the PET granules, and the critical values χ^2 for the lognormal distribution are 0.03 and 0.04 for the nylon 6,6 granules and the PET granules, respectively. The lognormal distribution thus provides a better fit than the Gaussian distribution to the experimental thickness data.

ζ-Potentials

ζ-Potentials are often used to characterize the electrical differences of the surfaces of materials in aqueous solutions. Figure 4 shows the zeta-potentials of the nylon 6,6 granules, PET granules, and granules coated with a chitosan layer as a function of the solution pH values. Chitosan-coated granules had positive ζ-potentials for pH < 6.6 and negative ζ-potentials for pH > 6.6, with the point of zero ζ-potential at pH about 6.6. This may be attributed to the amino groups in chitosan that acquired positive surface charges in an acidic solution by protonation, and negative surface charges in a basic condition possibly by deprotonation. In contrast, the ζ-potentials of nylon 6,6 granules and PET granules are significantly different from those of the granules coated with chitosan. It is seen from Figure 4 that the zero ζ-potential points for PET granules and nylon 6,6 granules are at pH about 2.3 and 3.4, respectively.
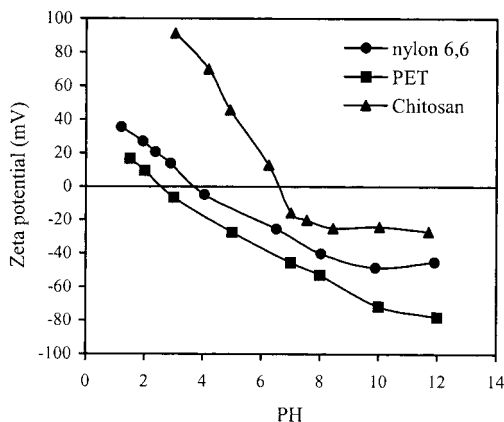
Figure 4 ζ-Potentials of nylon 6,6 granule, PET granule, and the coated chitosan layer versus solution pH values.
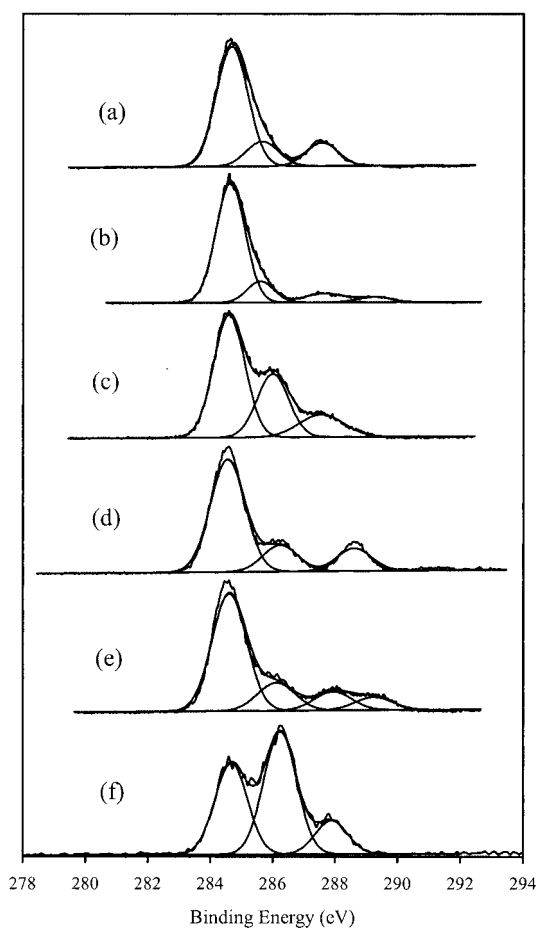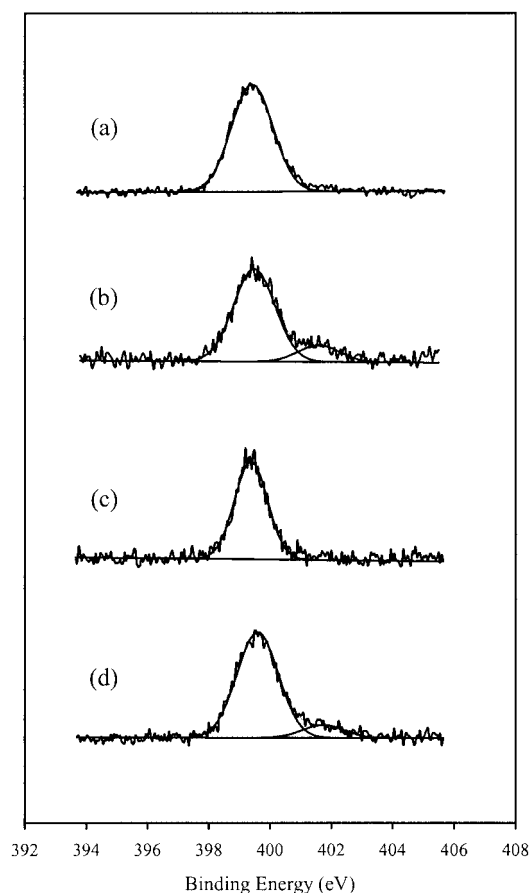
Figure 5 C1s XPS spectra of (a) nylon 6,6, (b) hydrolyzed nylon 6,6, (c) nylon 6,6 after peeling off the chitosan layer, (d) PET, (e) PET after peeling off the chitosan layer, and (f) the chitosan layer.

XPS spectra

The XPS spectra of the granules under various conditions are shown in Figure 5 and Figure 6. For nylon 6,6 granules, the C1s spectrum [Fig. 5(a)] can be fitted with three peaks at 284.6, 285.6, and 287.7 eV, respectively. The lowest binding energy peak at 284.6 eV is attributed to the C—C or C—H carbon atoms in the nylon 6,6 polymer chain and the higher binding energy peaks at 285.6 and 287.7 eV are attributed to the C—N and –CO—NH– carbon atoms, respectively. Only one peak (at 399.6 eV) is observed in the N1s core-level spectrum [see Fig. 6(a)] and this peak is attributed to the acylamino nitrogen atoms (–CO—NH–) present in the nylon 6,6 polymer. For PET granules, the C1s spectrum [Fig. 5(d)] can be fitted with three peaks at 284.6 eV for phenyl carbon atoms (–C_6H_4–, where C_6H_4 stands for benzene ring), 286.4 eV for methylene carbon atoms bound to one oxygen (–CH_2—O–), and 288.9 eV for ester carbon atoms (–CO—O–). The area ratio of these peaks is 67 : 23 : 20, which was close to the theoretical value from its molecular structure (60 : 20 : 20).

After hydrolysis, the nylon 6,6 granules were found to have a new peak at around 289 eV in the C1s spectrum [Fig. 5(b)]. This new peak may be attributed to the carboxyl carbon (–CO—O–), and thus suggests the production of carboxylic acid groups on the nylon surface during hydrolysis. This speculation is also supported by the decrease of the peak at 287.7 eV corresponding to the –CO—NH– carbon after hydrolysis. Because the relative intensity of the peaks at 287.7 and 289 eV was at about 2 : 1, it may be concluded that about 33% of the acylamino groups were hydrolyzed and turned into carboxyl groups. The C1s spectrum of hydrolyzed PET granules, however, did not show any noticeable difference from that of untreated PET granules (result not shown). This may be attributable to the binding energies of the C1s from the carboxyl groups on the hydrolyzed PET granules overlapping with that of the ester groups on the untreated PET granules.[22]
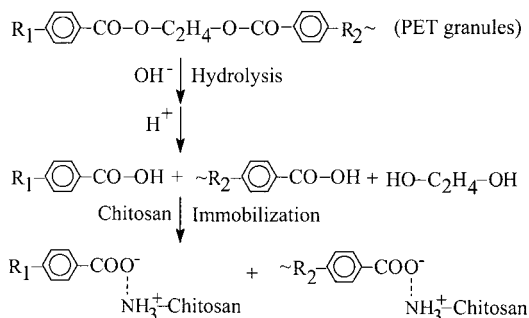
With a chitosan layer coated on the surface, the nylon 6,6 or PET granules had the same C1s spectrum with peaks at 284.6, 286.3, and 288.0 eV and a relative intensity ratio of 1 : 1.3 : 0.3, which are attributed to
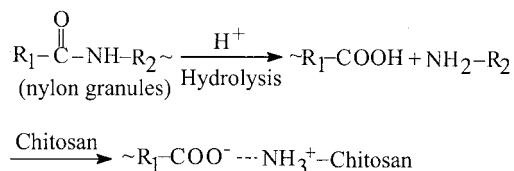

Figure 6 N1s XPS spectra of (a) nylon 6,6, (b) nylon 6,6 after peeling off the chitosan layer, (c) the chitosan layer, and (d) PET after peeling off the chitosan layer.

C—C or C—H carbon, C—N, C—O, or C—O—C carbon, and C=O or O—C—O carbon, respectively [Fig. 5(f)]. Because XPS with Al–K$_\alpha$ X-ray source usually can penetrate a depth only in the range of less than 10–20 nm,[23] and the average thicknesses of the chitosan layer immobilized on nylon 6,6 or PET granules were at 42.36 or 48.97 μm, respectively, it is therefore only the XPS spectra of the chitosan layer being observed for the nylon 6,6 or PET granules immobilized with chitosan. The N1s peak of the chitosan layer was located at 399.5 eV [Fig. 6(c)], which is attributed to the amino nitrogen (–NH$_2$) in chitosan.

It would be of interest to find out whether the coating or immobilization of chitosan on the nylon or PET granules is through physical or chemical interactions. The immobilized chitosan layer was carefully peeled off from the surface of the coated nylon 6,6 or PET granules and these granules were analyzed by XPS again. For the nylon 6,6 granules peeled off the chitosan layer, the C1s spectra show that the peak at around 286 eV, corresponding to C—N carbon, increased significantly [Fig. 5(c)], compared with that of hydrolyzed nylon 6,6 granules [Fig. 5(b)], but decreased greatly, compared with that of chitosan [Fig. 5(f)]. It is therefore believed that the carboxylic acid groups on the hydrolyzed nylon 6,6 granules bound with the amino groups of chitosan and formed salts (R–NH$_3^+$···$^-$OOC–) at the interface during the immobilization process. This is supported by the N1s spectra in Figure 6 where, in contrast with the single peak of nitrogen in chitosan [Fig. 6(c)], the N1s spectra of the nylon 6,6 granules peeled off the chitosan layer had a new peak at 401.6 eV [Fig. 6(b)], which can be attributed to the nitrogen in the salts of (–NH$_3^+$···$^-$OOC–), as a consequence of charge transfers occurring from the nitrogen atoms of chitosan to the oxygen atoms of the carboxylic groups on the hydrolyzed nylon 6,6 granules through an acid–base ionic binding. The hydrolysis process of the nylon 6,6 granules and the immobilization process of chitosan on the hydrolyzed nylon 6,6 granules is schematically proposed in **Scheme 1**.

$$R_1-\overset{O}{\overset{\|}{C}}-NH-R_2\sim \xrightarrow[\text{Hydrolysis}]{H^+} \sim R_1-COOH + NH_2-R_2$$
$$\xrightarrow{\text{Chitosan}} \sim R_1-COO^- \cdots NH_3^+-\text{Chitosan}$$

Scheme 2 Proposed hydrolysis and coating processes for PET granules.

For the PET granules peeled off the chitosan layer, the C1s peak at around 289 eV was largely reduced and a new peak at around 288 eV appeared [Fig. 5(e)]. Again, similar to the N1s spectra of the nylon 6,6 granules peeled off the chitosan layer, the N1s spectra of the PET granules peeled off the chitosan layer had a new peak at 401.6 eV [Fig. 6(d)]. These results therefore also suggest the formation of the salt structure of (R–NH$_3^+$···$^-$OOC–) between the hydrolyzed PET and the coated chitosan at the interface, probably attributable to the acid–base ionic binding between the carboxyl groups on the hydrolyzed PET granules and the amino groups in chitosan. The hydrolysis process of the PET granules and the immobilization process of chitosan on the PET granules is suggested in **Scheme 2**.

Therefore, the immobilization of chitosan on the hydrolyzed nylon 6,6 or PET granules is at least partly effected through chemical interactions.

CONCLUSIONS

Improving the mechanical property of chitosan has practical interest for chitosan to be potentially used as an adsorbent in water and wastewater treatment. This research investigated the approach to coat or immobilize chitosan on other granular materials such as nylon 6,6 or PET granules. A simple acid or base hydrolysis process was used as a pretreatment process for the nylon 6,6 and PET granules to improve or increase the adhesion of chitosan with these granules. It was found that chitosan can be effectively coated or immobilized on the hydrolyzed nylon 6,6 or PET granules through a covalent chemical interaction forming the salt structure of (–NH$_3^+$···$^-$OOC–) between the hydrolyzed granules and the coated chitosan at the interface.

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$$R_1-\text{⬡}-CO-O-C_2H_4-O-CO-\text{⬡}-R_2\sim \quad \text{(PET granules)}$$

OH$^-$ | Hydrolysis

H$^+$ |

$$R_1-\text{⬡}-CO-OH + \sim R_2-\text{⬡}-CO-OH + HO-C_2H_4-OH$$

Chitosan | Immobilization

$$R_1-\text{⬡}-COO^- \qquad + \quad \sim R_2-\text{⬡}-COO^-$$
$$NH_3^+-\text{Chitosan} \qquad\qquad NH_3^+-\text{Chitosan}$$

Scheme 1 Proposed hydrolysis and coating processes for nylon 6,6 granules.

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