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Polypyrrole-coated natural rubber latex by admicellar polymerization

Received: 3 August 2001
Accepted: 14 November 2001
Published online: 30 March 2002
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Abstract Admicellar polymerization has been used for the preparation of an electrically conductive polypyrrole coating on latex particles. An anionic surfactant, sodium dodecyl sulfate (SDS), was adsorbed onto natural rubber (NR) latex particles to form the surfactant bilayers after adjusting the pH below the point of zero charge of the latex surface. Adsorption of SDS and pyrrole adsolubilization were determined as a function of pyrrole and sodium chloride concentrations. Pyrrole caused a decrease in SDS adsorption at equilibrium. Sodium chloride increased the surfactant adsorption

and the pyrrole adsolubilization. Thermogravimetric results showed the presence of polypyrrole. The conductivity of the polypyrrole-coated NR latex film prepared by admicellar polymerization without salt was the lowest; however, with salt addition, the conductivity of the film improved significantly. The oxidative polymerization technique resulted in a relatively higher conductivity than oxidative admicellar polymerization.

Keywords Polypyrrole · Natural rubber latex · Surfactant · Admicellar polymerization · Conducting polymer

Introduction

Electrically conductive polymers have been investigated over the last 2 decades. The development of research on these polymers has been growing owing to their anticipated applications. Conducting polymers have been utilized in several fields, such as electronic devices and sensors [1, 2, 3]. Among these electrically conductive polymers, polypyrrole (PPy) has been studied most often owing to its high conductivity and thermal stability.

There is much activity to produce PPy for applications such as biological technologies [4, 5]; however, limitations of PPy, such as poor mechanical properties and poor processibility, must be addressed in order to achieve satisfactory utility. Conducting PPy can be obtained in various forms, like films and powders. Many preparative techniques have been examined, including electrochemical polymerization [6], chemical polymerization [7] and counterion-induced processibility

[8]. One method to apply this polymer is the thin-film technique referred to as admicellar polymerization [9, 10].

Admicellar polymerization is, by design, a fine-coating technique that leads to the formation of ultrathin polymer films on charged surfaces by using surfactant bilayers as a reaction template [11]. PPy films on nickel [11], alumina [12], and other substrates [13] have been synthesized by admicellar polymerization. Application of a thin PPy coating to a moldable latex might improve its utility by overcoming the poor processibility of neat PPy from its solubility and melt properties. Moreover, Yuan et al. [13] recently reported that the use of surfactant and admicellar polymerization significantly influences film thickness and structure and may offer advantages to other materials.

Most previous works report the preparation of PPy via electrochemical techniques with varying electrolyte and dopant to enhance conductivity and processibility.

Unlike admicellar polymerization where polymerized pyrrole can be located at the surface of porous substrates, the conventional technique provides an interpenetration of PPy in another polymer matrix. For example, Dufort et al. [14] have shown that electrochemical synthesis of PPy with an elastomeric latex (e.g., carboxylated elastomeric latex which acts as an electrolyte and a dopant) leads to the formation of PPy surrounded by latex particles with good interpenetration and uniformity, so conductivity is enhanced. Another route to prepare PPy composites by in situ polymerization (with oxidizing agent) in a suspension of polymeric powder or natural rubber (NR) latex has also been reported [15]. According to this work, the composites of PPy and NR latex were prepared with various types and amounts of surfactant (1–5 wt%) to prevent latex coagulation. Excess surfactant led to isolated PPy being formed in the aqueous phase and lower conductivity. Moreover, the effects of oxidant type and content (0.5–5 molar ratio) were obvious, i.e., 50 wt% pyrrole in the composite with chlorinated polyethylene powder using ferric chloride as an oxidant showed a conductivity of 0.5 S/cm, but if the oxidant is copper chloride, the conductivity is reduced markedly to less than 10^{-6} S/cm. However, by admicellar polymerization to form a PPy coating (about 10-nm thick) on the nickel flakes (50 g nickel, 20 mmol sodium persulfate, and 20 mmol pyrrole), its composite with polyethylene (as a matrix) showed an enhanced conductivity from 10^{-13} S/cm for a 1% volume fraction to about 10^{-3} S/cm at 15% volume fraction [11].

In this study, oxidative admicellar polymerization and oxidative polymerization without surfactant (which is similar to the in situ polymerization method) were used to produce thin films of a conducting PPy coating over latex particles (without varying the oxidant). This effort has two possible advantages: the processing of PPy might be facilitated and the electrical conductivity of the latex might be improved. Since the pyrrole polymerization is done in the latex or the emulsion, direct benefits for PPy processing may be achieved through existing knowledge on coatings, film casting, compounding, and so on. Moreover, the mechanically deformable rubber core may lead to a change in electrical conductivity in deformed and undeformed states (piezoelectric application) [15, 16]. Owing to its well-established structure, high interaction, and stability with several surfactants, NR latex was chosen as the substrate for PPy coating. The main focus in this work is to study the conditions for adsolubilizing pyrrole monomer onto the surface of latex particles with surfactant. Concentrating the monomer at the interface by partitioning it into an adsorbed surfactant bilayer changes the reaction conditions to be more favorable to the formation of ultrathin films [12]. After the polymerization had finished, excess surfactant was washed away with water

to obtain a thin PPy coating over the latex surfaces. The surfactant adsorption isotherm and pyrrole adsolubilization were determined in order to obtain a well-developed thin polymer film. The polymer film attached to the latex surface was also characterized to measure the success of the admicellar polymerization and associated improvements on conductivity.

Experimental

Materials

NR latex was provided by Ansell (Thailand) Company. Anionic sodium dodecyl sulfate (SDS) surfactant of 99% purity was obtained from Aldrich. Pyrrole of 97% purity was purchased from Merck and was purified by vacuum distillation and stored in a refrigerator at about 4 °C before using. High-performance liquid chromatography (HPLC) grade methanol of 99.8% purity was provided by BDH Laboratory Supplies. Ammonium persulfate from Merck and sodium chloride from Fluka were used without further purification. Sodium hydroxide from Fluka and hydrochloric acid from J.T. Baker were used for adjusting the pH.

Purification of the NR latex

NR latex particles were purified by centrifugation and were redispersed in distilled water several times to remove dissolved impurities. The resulting particles were considered to be clean. After washing, the particles were resuspended in water at a concentration of 14%.

Particle size measurement

The NR latex after purification was measured using a particle size analyzer. The lens employed in this project was 45 mm for the particle range 0.1–80 μm . The active beam length was set to 24 mm. The latex particles were placed in a sample cell across a laser beam. The instrument analyzed the average particle size and the standard size distribution from the laser beam obscuration depending on the beam length parameter. Consequently, the specific surface area was calculated from the particle diameter with the assumption of spherical particles of constant volume.

Electrophoretic mobility measurement

The change in the surface charge of latex particles with pH is important to determine the surfactant adsorption. Electrophoretic mobility was used to determine the surface charge of the latex particles at various solution pH. The NR colloidal dispersion was diluted in 250 ml distilled water. The pH in the solution was adjusted by 0.1 M NaOH or HCl, and was left to equilibrate for 1 day. The electrophoretic mobility of the latex particles was observed at room temperature with a ZetaMeter 3.0.

SDS adsorption isotherms and pyrrole adsolubilization measurement

SDS solutions (14 ml) of known concentration were adjusted to pH 3.0 with HCl. Then, the solution was added to a screw-cap test tube containing a 0.07 ml aqueous solution of latex (0.01 g dry weight). The tubes were agitated in a shaking bath at 30 °C while the SDS solution was allowed to equilibrate for 30 h. After that, a

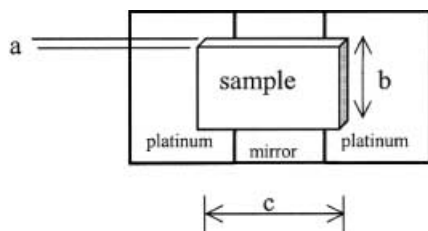
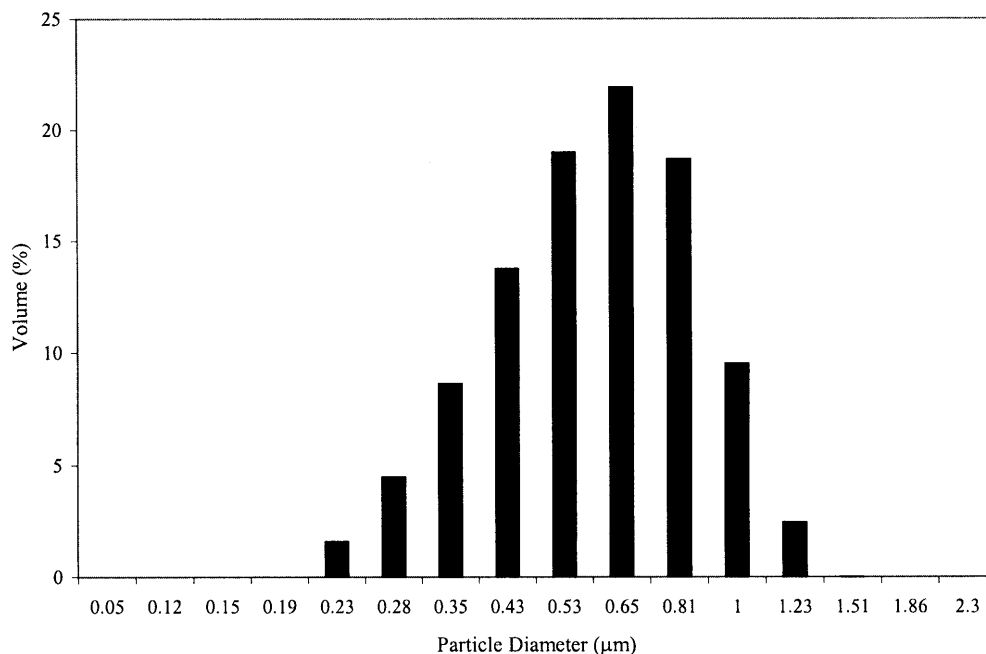


Fig. 1 Geometry of the conductivity measurement

7 ml solution of pyrrole and NaCl, whose concentrations were adjusted to attain the desired final concentrations, was lowered to pH 3.0 and then added to the tube. The combined solutions were agitated at 30 °C and left to equilibrate for 6 h. The latex particles were separated from solution by centrifuging and were filtered through a cellulose nitrate membrane of 0.2- μm pore size. The SDS concentrations after the removal of the latex particles were determined using a Hewlett-Packard 1050 high-performance liquid chromatograph with an Alltech conductivity detector. The HPLC column was a Nova-Pak phenyl reverse-phase column (Waters Division of Millipore). In order to obtain the SDS concentration accurately, two mobile phase solvents were used sequentially. First, 20 vol% methanol in water was passed through the chromatography column at 1 ml/min. After 4 min, the solvent mixture was changed to 100 vol% methanol at the same flow rate. Salt eluted from the first step and SDS from last step. The SDS concentration was determined by using a calibration curve between conductivity versus SDS standard concentration. Samples were run in triplicate and averaged. SDS adsorption after equilibration was calculated by the difference between the initial concentration before adsorption on the latex particles and the final concentration after adsorption.

Pyrrole concentrations after the removal of the latex particles were analyzed using a Hewlett-Packard 4950 gas chromatograph with a flame ionization detector. The gas chromatography column was a Hewlett-Packard fused silica capillary column (HP-1 cross-linked methyl silicone). The injection volume was 1 μl with a split ratio of 20:1 and with helium as the carrier gas.

Fig. 2 Histogram showing the particle size distribution by volume of the natural rubber (NR) latex



The determination of SDS adsorption isotherms and pyrrole adsolubilization was calculated Eq. (1):

$$\Gamma = \frac{(c_i - c_f)V}{A}, \quad (1)$$

where Γ is the amount of surfactant adsorbed to the surface particles or the amount of pyrrole adsolubilization inside the SDS bilayer (micromoles per square centimeter), c_i is the initial concentration of surfactant before adsorption or pyrrole before adsolubilization inside the SDS bilayer (micromoles per liter), c_f is the final concentration of surfactant after adsorption or pyrrole after adsolubilization inside SDS bilayer (micromoles per liter), A is the total particle surface area of the latex (square meters per gram), and V is the volume of the solution (millilitres).

The determination of the adsolubilization constant, K_{ads} defined by Wu et al. [10] was calculated from Eq. (2):

$$K_{\text{ads}} = \frac{(\text{moles of adsolubilized pyrrole per moles adsorbed SDS})}{(\text{concentration of pyrrole in the supernatant})}. \quad (2)$$

Polymerization of pyrrole onto latex particles

A 6.5 ml aqueous solution of NR latex (0.91 g dry weight) was prepared in the three tubes and 6.5 ml of the following solutions was added:

1. 10 mM pyrrole.
2. 10 mM pyrrole and 16 mM SDS.
3. 10 mM pyrrole, 16 mM SDS, and 0.6 M NaCl.

These solutions were maintained at 30 °C. After 30 min, an equimolar amount of ammonium persulfate (based on pyrrole) was added as the concentrated solution. After 4 h, the latex was rinsed with distilled water and filtered through the cellulose membrane, poured onto a flat sheet and dried at 60 °C in a vacuum oven. The morphology of the films was observed using an optical microscope.

Thermogravimetry was performed using a Du Pont Instruments TGA 2950 at a heating rate of 10 °C/min (30–600 °C) in a nitrogen atmosphere with a flow rate of 20 ml/min.

Fig. 3 The electrophoretic mobility of charged latex particles in aqueous solution at various pH

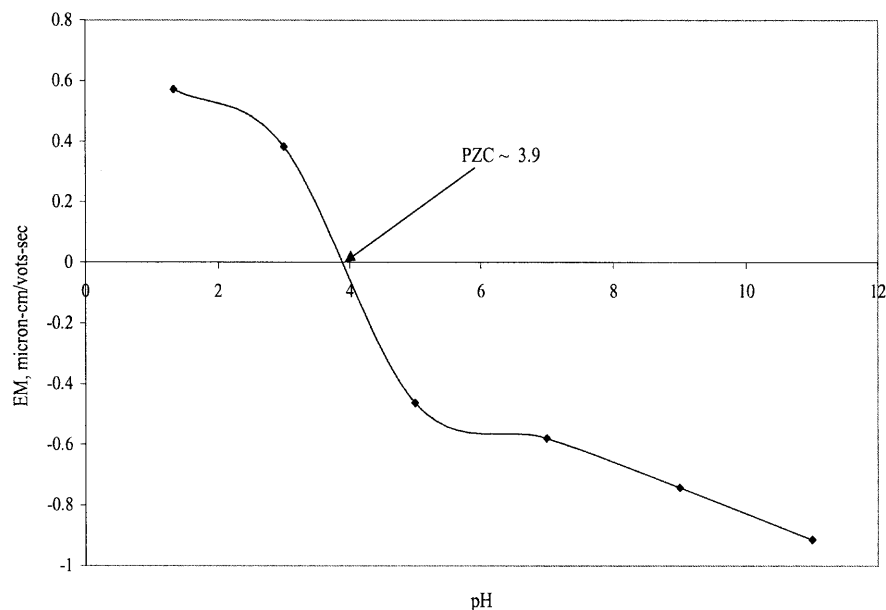
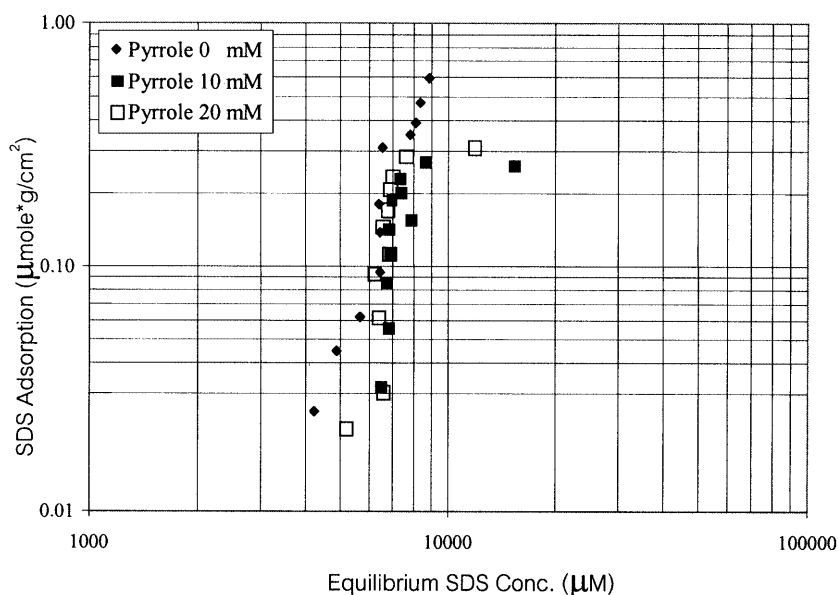


Fig. 4 Adsorption of sodium dodecyl sulfate (SDS) on latex particles at various pyrrole concentrations



Conductivity measurement

The geometry of the electrodes used to measure the conductivity of the samples is shown in Fig. 1. The device comprised three layers: a nonconducting mirror, a titanium layer deposited on both sides of the mirror, and thin layers of platinum on top of the titanium layers. These layers were connected to each other where platinum and titanium were placed on the edge of the mirror. Films of the modified latex were placed on the top of the electrode; they touched the layer platinum and the mirror.

The thickness of the latex films ranged from 0.005 to 0.008 cm. A voltage from a power supply was applied to the electrode and the current was measured using a picoammeter. The resistance, R , of

the films was calculated using Eq. (3) and the conductivity was found using Eq. (4):

$$R = \frac{V}{I}, \quad (3)$$

$$\rho = \frac{1}{\sigma} = \frac{Rab}{c}, \quad (4)$$

where R is the resistance (watts), V is the voltage (volts), I is the current (amperes), ρ is the resistivity (ohm centimeters), σ is the conductivity (siemens per centimeter), a is the film thickness (centimeters), b is the film width (centimeters), and c is the film length (centimeters).

Fig. 5 Adsorption of SDS on latex particles at various salt concentrations. The initial pyrrole concentration was 10 mM in all cases

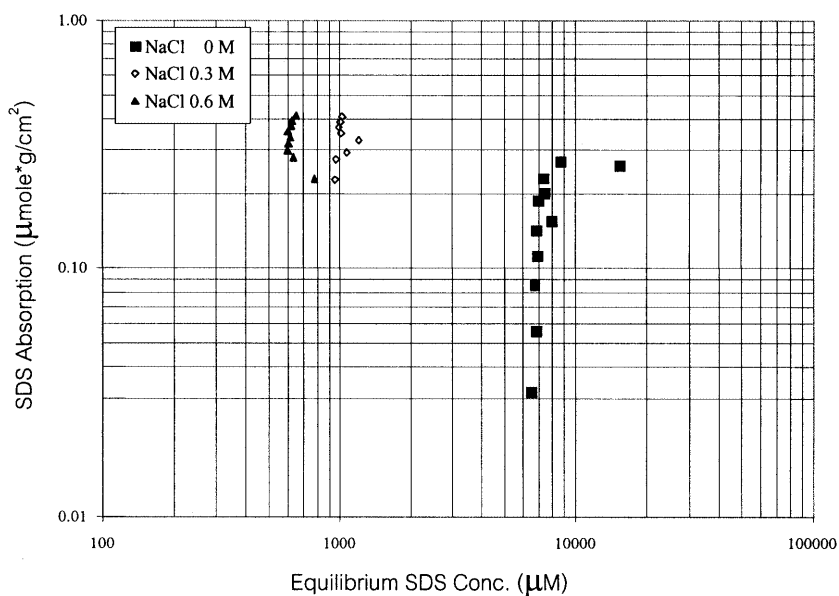
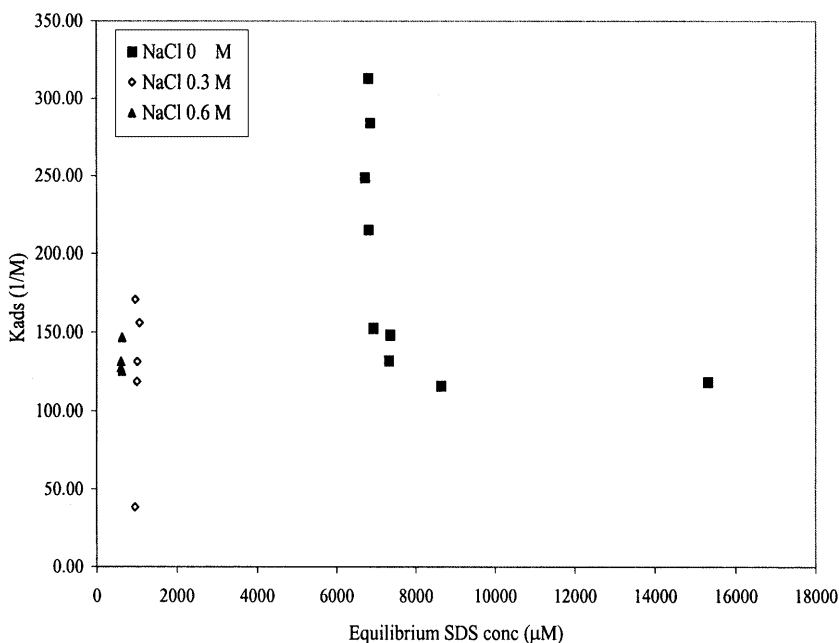


Fig. 6 Adsolubilization constant of pyrrole in SDS admicelles onto latex particles with various salt concentrations. The initial pyrrole concentration was 10 mM in all cases



Results and discussion

The volume distribution of the NR latex after purification is shown in Fig. 2. The particle size analysis shows that the NR latex particles have a diameter of $0.63 \pm 0.42 \mu\text{m}$ and specific surface area of $9.7 \text{ m}^2/\text{g}$. This result compares well to values from the literature [17, 18] and indicates that the NR latex is naturally polydisperse. The surface charge of the latex can be found from the electrophoretic mobility, the movement of the colloidal particle under an applied electric field.

The electrophoretic mobility of the colloidal dispersion of the NR latex with various pH of the solution is illustrated in Fig. 3. The net surface charge of zero (or the point of zero charge, PZC) is known from the intersection of the electrophoretic mobility curve and the zero axis. As shown in this figure, the net zero charge on the surface of these NR latex particles is found at pH 3.9 at room temperature. At pH values below the PZC, the latex particle exhibits a positive charge, while above the PZC, the charge of the surface becomes negative.

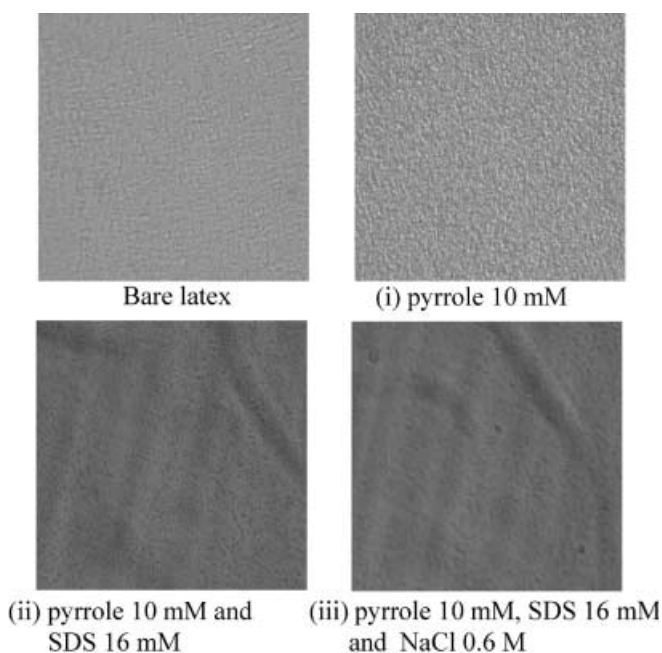


Fig. 7 Optical microscope images of NR latex particles

These electrophoretic mobility results determine the type of surfactant adsorbed on the latex surface. Anionic surfactants are adsorbed below the PZC, while cationic surfactants are adsorbed above the PZC. In this study, the anionic surfactant SDS was employed so the pH was adjusted to 3. SDS was particularly attractive because there was a precedent for its use in the polymerization of pyrrole. SDS adsorption was measured with various pyrrole concentrations as shown in Fig. 4. The adsorption isotherm of SDS on NR particles (without pyrrole) illustrates the region of surfactant bilayer formation (fast adsorption) starting from the equilibrium concentration of SDS about $4,500 \mu\text{M}$ and no plateau region is seen within the range of the SDS concentration of interest. When pyrrole monomers were added, the adsorption isotherms showed a region of bilayer formation within the equilibrium concentration of SDS around $6,000\text{--}7,300 \mu\text{M}$, which corresponded to an initial concentration of SDS at $6,600\text{--}21,000 \mu\text{M}$. Beyond this region, there is a slow adsorption region followed by a plateau region (no more adsorption), which is the region where micelles can be formed. Pyrrole causes a decrease in surfactant adsorption in accord with prior work [12]. Both pyrrole concentrations at 10 and 20 mM give similar results for the SDS adsorption isotherm. Figure 5 illustrates that the salt overwhelms the effect of pyrrole on the adsorption isotherm of SDS. Salt improves the SDS adsorption, even a low salt concentration, as observed previously by Wu et al. [10]. The effect of salt on the adsolubilization constant, K_{ads} , of pyrrole in SDS admicelles is shown in Fig. 6. The value of K_{ads} is

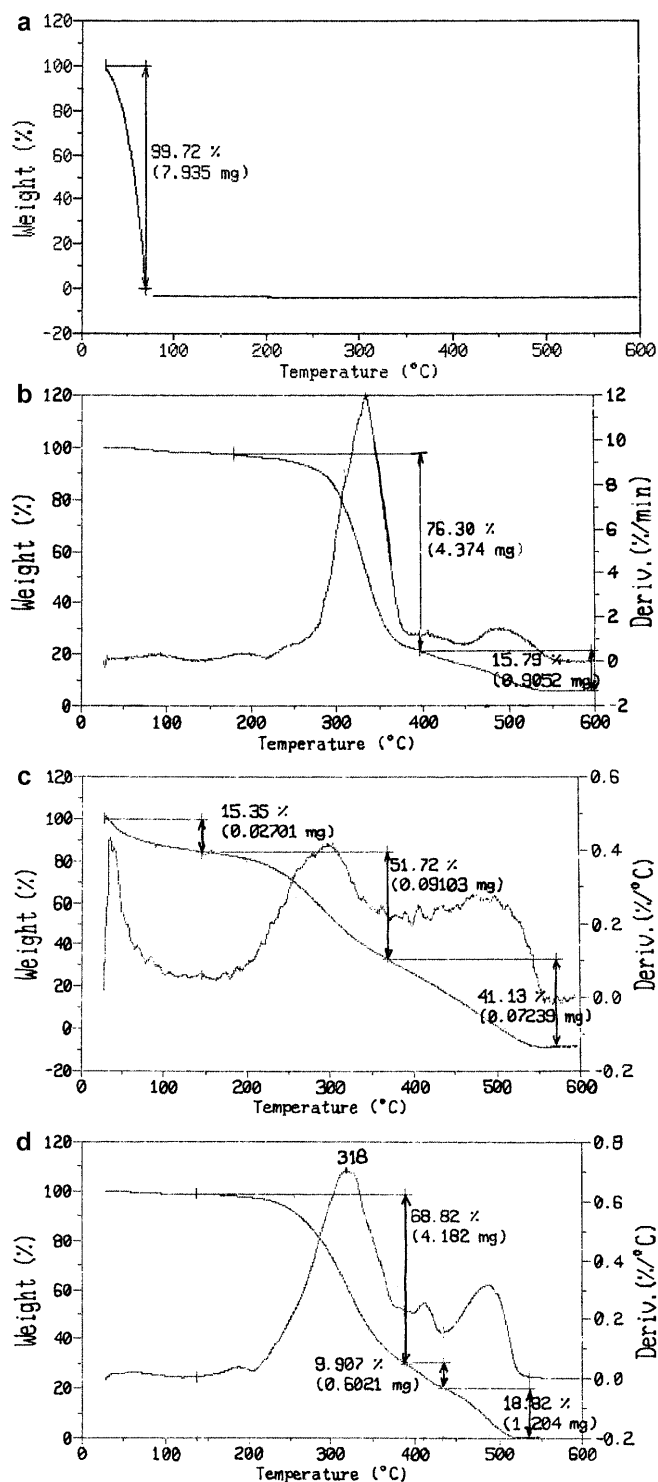


Fig. 8 Thermogravimetric analysis thermograms from 30–600 °C for **a** pure pyrrole, **b** pure NR, **c** pure polypyrrole, and **d** admicellar polymerized polypyrrole-coated NR latex particles

found to decrease with increasing SDS concentration. However, while the value of K_{ads} decreases, the pyrrole adsolubilization increases with increasing SDS concen-

tration because the amount of surfactant at the interface rises so rapidly. Similarly, the adsolubilization of pyrrole increases with the addition of salt. Funkhouser et al. [12] hypothesized that pyrrole is a highly hydrophilic species which adsolubilizes in the headgroup region in the bilayer. The increasing surfactant adsorption with increasing salt means higher coverage and the creation of more headgroup sites for adsolubilization. The salt decreases electrostatic repulsion between headgroups, which allow more adsorption and adsolubilization. At this point, the selected conditions for admicellar polymerization of pyrrole onto the NR particles are at 10 mM pyrrole and 16 mM SDS (oxidant ratio kept constant as a fixed parameter at a pyrrole/ammonium persulphate 1:1 molar ratio) at pH 3.0 (just below the PZC of NR latex particles to avoid NR agglomeration). These amounts of pyrrole and SDS are relatively lower than those used in admicellar polymerization on the solid polar substrates and in situ polymerization techniques [11, 12, 13, 14, 15].

Admicellar polymerization of pyrrole to form PPy film on the NR latex particles was performed from three solutions of pyrrole, pyrrole and SDS, and pyrrole, SDS, and salt. The morphological structures of the dried NR latex before and after coating with PPy are shown in Fig. 7. This figure shows the fine size (about a micron or less) of the rubber particles (magnification of 1000 \times) and their random distribution in all the samples; however, the texture of the NR with 10 mM pyrrole (Fig. 7a) prepared by a simple mixing (without surfactant) is rather rough with obvious dark domains of PPy. On the other hand, the samples of NR coated with PPy by admicellar polymerization, in Fig. 7c and d, exhibit

smooth textures (especially when salt is added) with finer domains.

Thermogravimetric analysis results in Fig. 8 a reveal that pyrrole degrades continuously when the temperature increases from room temperature and totally vanishes at about 75 °C. NR shows the major decomposition at a peak temperature of 336 °C and minor decompositions at elevated temperature (Fig. 8b, Table 1), while PPy shows its characteristically board decomposition that may separate into two decomposition peaks around 300 and 490 °C (Fig. 8c). It is clearly seen from Fig. 8d that pyrrole in sample 2 was converted to PPy completely because there was no trace of residual pyrrole at temperatures below 100 °C (note that the polymerization was done at 30 °C to ensure that pyrrole was not degraded before being polymerized). Importantly, the peak degradation temperatures of the sample are seen at 318 (board peak covering both first PPy and NR decompositions), 412, and 490 °C, corresponding to the decomposition of PPy and NR. A comparative thermogravimetric analysis result (decomposition temperature range of 380–440 °C) was also found in a PPy/NR composite made from in situ polymerization [15]. This ensures the presence of PPy in the sample or the success of admicellar polymerization of pyrrole on the NR latex substrate.

The conductivity of the film is presented in Table 2. In sample 1 without SDS, PPy appeared to distribute in an aqueous solution of NR latex and was not adsorbed onto the latex particles; therefore, a rough texture was seen. In other words, this sample has no surfactant to act as an emulsifier for PPy coating onto the latex particles. The electrical transport of PPy is relatively good

Table 1 Degradation temperatures according to Fig. 8a–d

Materials	First degradation		Second degradation	
	Peak temperature (°C)	Decomposed mass (%)	Peak temperature (°C)	Decomposed mass (%)
Pyrrole	Continuously degraded from 26 to 75 °C	99.72	None	None
Natural rubber ^a	336	76.30	490	15.79
Polypyrrole ^b	306	67.07	481	41.13
Admicellar polymerized polypyrrole-coated natural rubber latex particles ^a	318	78.73	489	18.82

^a There is a small peak at the middle (412 °C) between both degradation peaks in the thermograms of natural rubber and admicellar product

^b 100% mass decomposition, although combined decomposed mass is greater than 100%

Table 2 Polymerization conditions and the characteristics of polypyrrole with natural rubber latex particles. The initial pyrrole concentration was 10 mM in all cases

No.	SDS concentration (mM)	NaCl concentration (mM)	Conductivity $\times 10^{-6}$ (S/cm)	Color
1	0	0	2.062	Brown
2	16	0	0.959	Black
3	16	0.6	1.449	Black

(2×10^{-6} S/cm) because PPy is distributed throughout the dried film to allow electrical conductivity. Our result is closed to that found by Xie et al. [15]. According to this work, the PPy/NR composites made from in situ polymerization show a conductivity of 10^{-5} S/cm at 1.2 wt% surfactant and 1:1 molar ratio of oxidant/monomer, while the maximum conductivity of 10^{-1} S/cm was found at the optimum amount of surfactant (2.5 wt%) and a molar ratio of oxidant to monomer of 2.5. In sample 2 produced from drying a solution of pyrrole and SDS without salt, the conductivity is reduced by half. Thus, the presence of SDS seems to reduce the electrical transport, probably by formation of a thinner coating [12]. As stated earlier, when there is no salt, the repulsion of SDS headgroups is maximized and the pyrrole adsolubilization is minimized owing to the poor hydrophobicity. This may cause the reduction of adsolubilization of pyrrole around the latex particles. In addition, the connectivity of PPy is relatively poor and the less uniform distribution of PPy on the latex surfaces can cause the poorer conductivity [15]. Sample 3 was obtained from a solution of pyrrole, SDS, and salt. It shows increased conductivity of about 50% compared to that of sample 2. The addition of salt improves the adsolubilization of pyrrole in the SDS admicelles by reducing the repulsion, so more pyrrole is adsolubilized and coated more homogeneously onto the latex surface and the conductivity is enhanced. Defects might be formed where some of the NR latex particles were not coated by PPy. However, the low initial pyrrole

concentration (about 0.5 wt%) coupled with the wide distribution of the NR particle size and shape might contribute to the low conductivity of all the samples [18]. It is interesting to note that only a small content of PPy coating can enhance the conductivity of NR by several orders (the conductivity of pure NR is close to that of polyethylene, which is about 10^{-13} S/cm [11]).

Conclusions

Admicellar polymerization can be adapted for a latex with surfactant molecules forming bilayers on the surface of the latex particles in aqueous solution. The method was employed to form thin PPy films on the charged surface of NR. The NR latex exhibits a PZC at 3.9 so anionic surfactant, SDS, was chosen with the solution pH adjusted to 3.0. Pyrrole causes a decrease in surfactant adsorption. Suitable contents of SDS and pyrrole for admicellar polymerization are 16 and 10 mM, respectively. The presence of a small amount of salt, sodium chloride, substantially improves the surfactant adsorption and pyrrole adsolubilization. A PPy-coated NR latex prepared in the absence of surfactant exhibited slightly higher conductivity than a PPy-coated latex prepared with surfactant with or without salt.

Acknowledgements The authors thank The Development Grant for New Faculty/Researchers from Chulalongkorn University for financial support and Ansell for providing the NR latex solution.

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