Poly-L-lysine/carboxymethylcellulose multilayers on corona treated polypropylene substrates♣

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Poly-L-lysine/carboxymethylcellulose multilayers were formed by a self-assembly deposition technique on negative corona charged polypropylene (PP) films by consecutive dipping of these PP films in acidic solutions of poly-L-lysine (PLL) and carboxymethylcellulose (CMC). The binding of the biopolymers was irreversible over the time of the deposition. The films were examined by spectroscopic (FTIR, NIR and UV-VIS), electrical, optical and rheological methods. The transmittance spectra of the films with multilayers indicated the presence of PLL and CMC. The intensity of the typical bands was found to increase as the number of the deposited layers grew. The adhered multilayers changed the electrical impedance of the PP films. The multilayers were stable in distilled water and their equilibrium degree of swelling increased with the increase of the number of adhered layers. The tensile modulus of the coated films in the dry and hydrated states was found to increase with the increase of the number of adhered layers.

1. Introduction

In the past decades, the field of nanostructured material formation has progressed significantly. Self-assembly processes of polymers involving electrostatic interactions can be used to build-up multilayered materials with unique properties [1, 2]. Multilayer fabrication is based on the deposition of polyelectrolytes on charged surfaces and interfaces. Provided that each deposition step leads to surface charge inversion, the subsequent deposition finally results in a layered complex, stabilised by strong electrostatic forces [3]. To ensure multilayer growth, the polyelectrolyte deposition process must be irreversible [4].

Although a great part of the polyelectrolyte deposition has been done on non-activated substrates, which are assumed to be negatively charged because of oxidation from the air, just a few studies on preliminarily substrate treatment have been reported. Different methods for surface modification have been attempted, such as plasma-treatment techniques and corona discharges [5, 6].

This work aims to investigate the fabrication and properties of multilayers from biopolymers on corona treated polypropylene substrates.

2. Experimental

2.1 Materials

We investigated isotactic polypropylene (PP) films produced by "Assenova Krepost" LTD. The film thickness was 20 μm. PLL hydrobromide BioChemika, molecular weight 70,000-150,000, and CMC sodium BioChemika, medium viscosity, were bought from Fluka and used without further purification or characterization. All other chemicals were of analytical grade.

2.2 Sample preparation

The corona treatment of the PP substrates was done in a point-to-plane three-electrode corona discharge system

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consisting of a corona electrode (needle), a grounded plate electrode, and a metal grid placed between them. A voltage of -5 kV was applied to the corona electrode and -1 kV to the grid. The samples were charged at a temperature of 30 °C for 5 minutes.

The corona pre-treated PP film was immersed in 1 wt.% PLL in NaOH solution (0.01 M NaOH and 0.1 M NaCl) for 15 min and dried in air for a few minutes. The deposition process was continued by consecutive dipping of the substrates for 15 min in 1 wt.% CMC and 1 wt.% PLL in an acetate buffer (pH 5.6 and ionic strength 0.1 M), and rinsing in distilled water. After that, the films were dried at room temperature for 48 h.

2.3 Sample characterization

The FT-IR transmittance spectra of the samples were measured by a Perkin–Elmer 1750 Spectrometer in the $(400 – 3000)$ cm^{-1} $((25000 – 3300)$ nm) spectral range, to an accuracy of 4 cm^{-1}. The transmittance in the spectral range from 200 nm to 3300 nm was measured by a Cary 05E spectrophotometer (USA), 0.1% accuracy).

The refractive indices (RI) were measured by the method of the disappearing diffraction pattern [7–9] using a laser refractometer at wavelengths of 532 nm and 632.8 nm with an experimental uncertainty of $\pm 5.10^{-4}$. As the evanescent field penetration depth is less than 1 μm [10], the measurements of the RI were performed in a surface layer with a thickness of about 1 μm.

The swelling tests were carried out in distilled water until constant weights of the films were achieved. The deposited layers were stable over the time of swelling and their equilibrium swelling degree was determined by the formula:

$$w = \frac{m - m_0}{m_0} \qquad (1)$$

where m is the sample weight at equilibrium swelling and m_0 is the weight of the dry sample.

The physicomechanical properties of the multilayers in both the dry and hydrated state were examined by simple extension at a constant deformation rate of 0.1 mm/s by a Stable Microsystems® Texture Analyzer (TAXT2i). The samples (dry film dimensions 10 mm×4 mm×0.02 mm) were glued to the metal holders by a cyanoacrylate adhesive. The Young's modulus was determined from a stress-strain curve for deformations less than 3%.

The magnitude and phase angle of the impedance were measured by a HP 4284A LCR meter, equipped with two ECG electrodes (Fiab Spa). The impedance spectra were determined in the frequency range 10 Hz to 1 MHz, at a 0.2 V measuring voltage.

3. Results

The FT-IR transmittance spectra of the PP films with different numbers of deposited layers in the 3000 –

500 cm^{-1} spectral range, Fig. 1, showed that the intensity of the absorbance band at 1456 cm^{-1} was independent of the presence of the layers. Therefore, it was taken as a reference. Two new bands appeared at 1580 cm^{-1} and 1650 cm^{-1}.
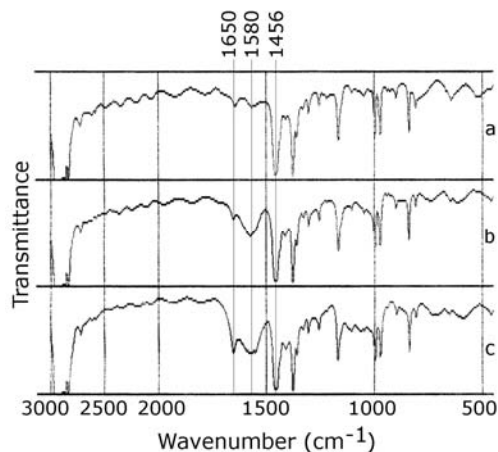

Fig. 1. FT-IR spectra of multilayer structures: a) 4 layers; b) 10 layers; c) 16 layers.
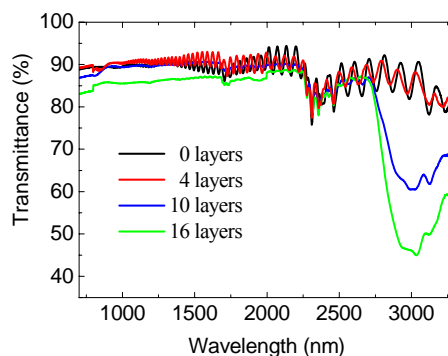

Fig. 2. NIR spectra of multilayer structures.

New bands, which were missing in the PP NIR transmittance spectrum, were observed at 3060 and 3125 nm – Fig. 2.

The measurements of the surface RI, performed in a surface layer with thickness of about 1 μm by the laser refractometer at wavelengths of 532 and 632.8 nm, gave the average effective values with different substrate and multilayer impacts (Fig. 3).
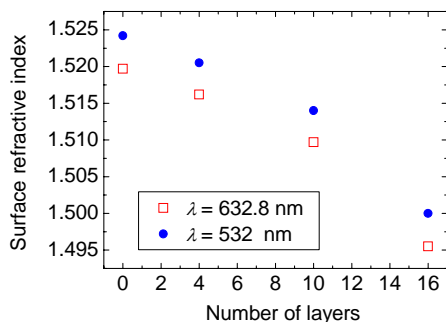
Fig. 3. Surface refractive index as a function of the number of layers.
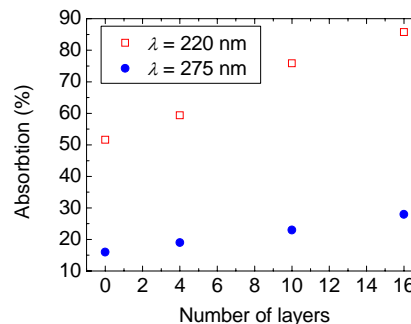

Fig. 5. UV absorption of PP/PLL/CMC films as a function of the number of layers.

4. Discussion

The characteristic band in the FT-IR spectra at 1580 cm^{-1} (fig. 1), which is due to carboxylate carbonyl [11], could be used as proof of the deposition of CMC. The band at 1650 cm^{-1}, due to amide-I [12, 13], indicates the presence of PLL.

The intensity of the typical bands was found to increase with the increase of the number of deposited layers – Fig. 4. Therefore, an assumption could be made that the binding of PLL and CMC on the surface is , and the amount of the bound compounds increases during the process of layer deposition.
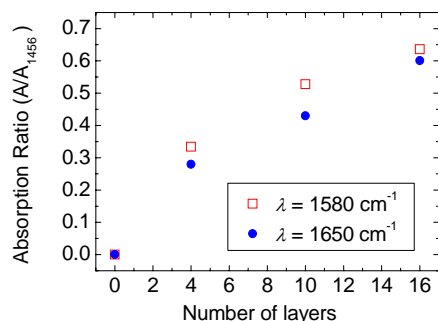

Fig. 4. IR absorption as a function of the number of layers.

The UV spectra also indicate that the absorption of the films at 220 and 275 nm grows with the increase in the number of layers (Fig. 5).

In the mid IR spectral range, we observed two absorption maxima (Fig. 2). The absorption maxima at 3268 and 3200 cm^{-1} indicate NH-CO (amide-I) for two PLL conformations at the β-sheet and the random coil structure type respectively [14]. As just the first PLL layer was built from an alkaline medium (pH 11) and possesses the β-sheet conformation, the proportion of the random coil structure increases with the increase of the number of layers.

When multilayer samples with different layer RI were investigated by the laser refractometer, the average RI n_s over the thickness d_p was measured, and the following relations were valid:

$$d_p \frac{n_s^2 - 1}{n_s^2 + 2} = d \frac{n^2 - 1}{n^2 + 2} + \frac{N}{2}\left(d_1 \frac{n_1^2 - 1}{n_1^2 + 2} + d_2 \frac{n_2^2 - 1}{n_2^2 + 2} \right)$$

(2)

$$d_p = d + \frac{N}{2}(d_1 + d_2)$$

where d_p is the average evanescent wave penetration depth during total internal reflection, calculated earlier [10]; N is the number of layers; d_1, n_1 are the thickness and RI of the first layer (PLL); d_2, n_2 are the thickness and RI of the second layer (CMC); d is the thickness of the PP substrate for evanescent wave penetration; and n is the RI of the charged PP substrate.

When the number of layers in the multilayer samples increases, the PP substrate RI impact decreases. The RI values for $\lambda = 532$nm are $n_1 = 1.45$ [15]; $n_2 = 1.515$ [16], and $n = 1.524$. Therefore, according to equation (2), the surface RI of the multilayer samples decreases with the increase of the number of layers, as shown in Fig. 3.

An indirect method for verifying the multilayer build-ups is film swelling in distilled water. PP is a hydrophobic material and it could not be hydrated. The presence of multilayers leads to a dramatic change in the swelling properties of the composites. The equilibrium swelling degree was found to increase with the increase of the number of layers, as shown in Table 1. This relation is correlated with the increased amount of hydrophilic biopolymers and demonstrates that the adhered layers are stable in aqueous solutions.

Table 1. Experimental swelling data.

Number of layers	0	4	10	16
Equilibrium degree of swelling (%)	0	11	32	58

Adhered multilayers change the electrical properties of PP films – the electrical impedance magnitude

decreases with the increase of the number of layers (Fig. 6). At the same time, the phase angle of the system increases. Therefore, the presence of the layers causes the electrical resistance increase and the reactance reduction.
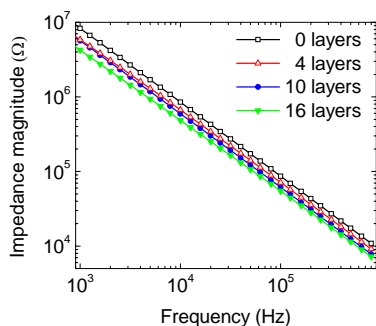

Fig. 6. Impedance spectrum of multilayer structures.

A possible application of the multilayer structures is their use as a packaging material. This was why we examined their mechanical properties.
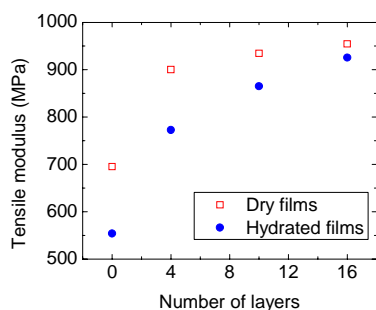

Fig. 7. Tensile modulus of multilayer structures as a function of the number of layers.

The tensile modulus values (Fig. 7) demonstrate that the built layers increase the mechanical strength in both the dry and hydrated states.

5. Conclusions

Polyelectrolyte multilayers from PLL and CMC on corona charged PP films were successfully fabricated. The optical, electrical, hydrophilic and mechanical properties of the structures were changed in a way that the polyelectrolyte behaviour of the deposited biopolymers explains.

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