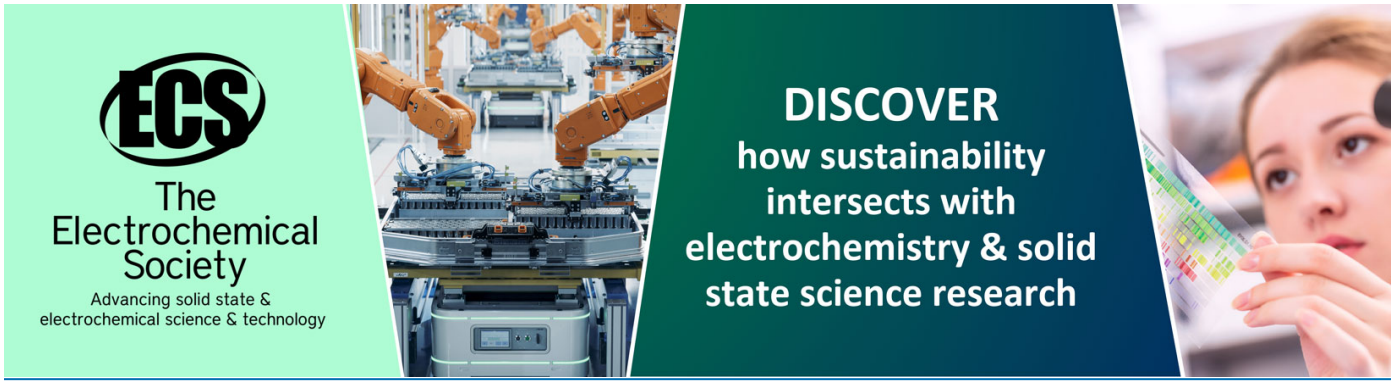
Mechanism of HF condensive complex plasma modification of polyurethane membrane coatings in the air environment



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Mechanism of HF condensive complex plasma modification of polyurethane membrane coatings in the air environment

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Abstract. The mechanism of the high frequency condensive complex plasma modification of polyurethane membrane coatings in air is investigated. The study revealed that after plasma modification in air, oxidation and hydrolysis of polyurethane membrane coatings occurs, which is expressed in an increase in the intensity of absorption bands corresponding to primary OH groups in the range of wave numbers 1005–1070 cm^{-1}, 1310 cm^{-1} and 1420 cm^{-1}, as well as in partial destruction of polyurethane chains with the formation of urea groups, which corresponds to the vibrations of CO-groups in the range of wave numbers 1590–1690 cm^{-1}.

1. Introduction

Due to the development and improvement of technologies in the textile and light industry, fabrics with a membrane coating have become widespread among consumers.

In the modern sense, "membrane" is either the thinnest film that is laminated (welded or glued using a special technology) to the fabric, or a coating applied in a liquid form to the fabric in the hot way [1]. On the inside, the membrane can be protected by another layer of fabric. From the outside, the material is waterproof, but if there is a difference in the partial pressure of water vapor under clothing and outside, the body evaporates. Thus, the use of new polymer compositions and improvement of coating compositions led to the creation of fabrics that have high protective and improved hygienic and operational properties, which contributes to the production of high-quality and comfortable products for workwear, tourism and outdoor activities.

Despite the uniqueness and versatility of membrane tissues, there is a number of disadvantages, such as low vapor permeability of non-porous membrane coatings, low strength and high cost of porous coatings. In this paper, we study membrane tissues with a non-porous membrane coating, due to the fact that they are widespread among the largest domestic manufacturers of textiles for special clothing. To eliminate the disadvantages associated with reduced hygienic properties, the HF condensive complex plasma modification was applied in air, which made it possible to improve these

properties [2–5]. In this work, the mechanism of the HF CCP modification of non-porous membrane coatings in air is investigated.

2. Materials, methods and equipment

The object of the study was a polyurethane (PU) membrane coating Climate 3 applied to fabric art. 80304 Climate 150 RS (100% polyether) with oil-water-repellent impregnation produced by Ltd. «TK Tchaikovsky Textil», Tchaikovsky city.

The modification was carried out in an experimental-industrial high frequency condensive plasma unit [6]. The modes of plasma modification were regulated by varying the parameters: plasma-forming gas consumption (G) 35 g/s, power (W_p) 1–1,5 kW, working pressure in the discharge chamber (P) 21–27 Pa; generator frequency (f) 13,56 MHz, processing time (τ) 5–20 min. Air was used as a plasma gas.

Changes in the chemical composition of PU coatings after plasma modification in air were studied by IR Fourier spectroscopy on an FSM-II 1202 spectrometer with the addition of multiple impaired total internal reflection (multiple violation of total internal reflection): in the range of wave numbers 650-4000 cm^{-1}.

3. Results

IR spectra of the control and modified samples of PU membrane coatings Climate 3 are presented in Fig. 1.

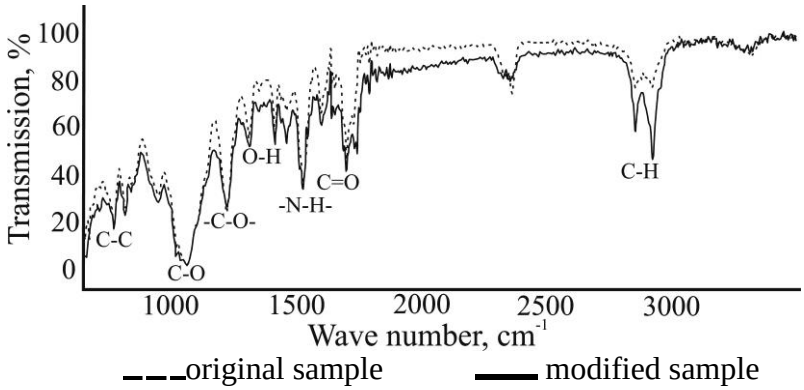


Figure 1. IR spectra of the control and modified PU coating Climate 3 (HF-plasma modification mode: W_p = 1.5 kW, P = 22 Pa, τ = 15 min, G = 35 g/s, plasma-forming gas - air)

The spectra of PU membrane coatings of the control and modified samples (Figure 1) demonstrate characteristic absorption bands for PU compounds [7–11]:

- absorption bands corresponding to the vibrations of the primary OH groups in the range of 1005–1070 cm^{-1} (in this case they appear due to the plasma treatment destruction);
- absorption band corresponding to asymmetric stretching vibrations of ether groups in PU in the range of 1210 cm^{-1};
- absorption bands corresponding to planar deformation vibrations of OH groups superimposed on fan vibrations of CH groups in the range of 1310 cm^{-1} and 1420 cm^{-1};
- absorption bands corresponding to the deformation vibrations of the N–H– urethane groups, manifesting themselves in the range of 1524–1526 cm^{-1};
- absorption band characteristic of the C=O groups in carbamide groups in the range of 1590-1690 cm^{-1};
- absorption bands corresponding to the C=O stretching vibrations of urethane groups, manifesting themselves in the range of 1700–1740 cm^{-1};

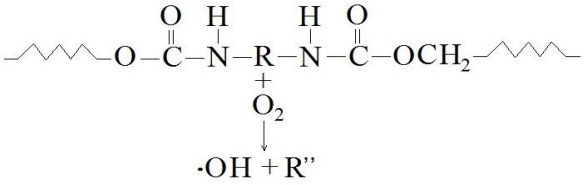
- absorption bands corresponding to C–H stretching vibrations in methylene groups in the range of 2858–2924 cm^{-1};

- absorption bands corresponding to –NH- vibrations in amides in the range of 3300–3350 cm^{-1}.

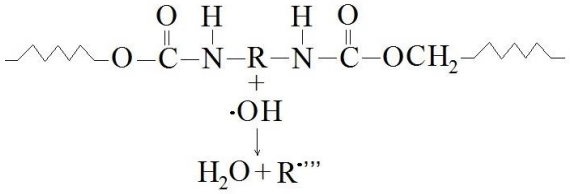
Based on the results obtained by IR spectroscopy, it can be assumed that the mechanism of the HF CCP modification of PU membrane coatings in air lays in the following:

- destruction of intermolecular hydrogen bonds of the surface layer of the membrane with the release of hydrogen-containing functional groups, such as NH or NH_2 groups with the subsequent formation of amine salts [12], which is reflected in an increase in the intensity of the absorption bands in the range of 2858–2924 cm^{-1}, as well as partial destruction of intramolecular bonds with the release of urethane groups, which corresponds to an increase in the intensity of the absorption bands in the range of 1524–1526 cm^{-1};

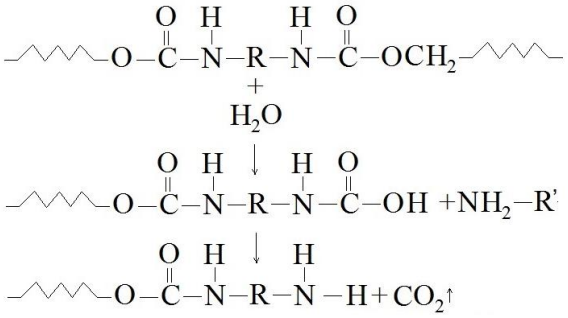
- oxidation, which is reflected in the an increase in the intensity of absorption bands corresponding to the primary OH groups in the range of wave numbers 1005–1070 cm^{-1}, 1310 cm^{-1} and 1420 cm^{-1} and which are accompanied by the following processes:



- the formation of free active radicals



- hydrolysis of a thin surface layer of the membrane, consisting in partial destruction of PU chains with the formation of carbamide groups, which corresponds to vibrations of CO-groups in the range of wave numbers 1590–1690 cm^{-1}. Presumably, the following processes occur:



4. Conclusions

Thus, it has been established that the HF condensive complex plasma modification in air leads to partial oxidation and hydrolysis of PU membrane coatings, which is expressed in an increase in the intensity of absorption bands corresponding to primary OH groups, in partial destruction of PU chains with the formation of carbamide groups, destruction of intermolecular hydrogen bonds of the surface layer of the membrane with the release of hydrogen-containing functional groups, such as NH or NH_2 groups, followed by the formation of amine salts and partial destruction of intramolecular bonds with the release of urethane groups.

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