

Plasma polymerized acrylic acid and formation of COOH-rich polymer layers in the presence of CO₂ gas

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Abstract: In contrast to most of the existing literature on plasma polymerization of acrylic acid (AA), not only the chemical structure of the deposits were studied, but also a new way to obtain COOH-rich surfaces. Therefore, acrylic acid/CO₂ polymer films with a thickness of ca. 150 nm were deposited in the pulsed plasma regime onto polyethylene and aluminium substrates.

Keywords: polyacrylic acid, -COOH-rich, plasma polymerization, dielectric properties

1. Introduction

Plasma polymerized acrylic acid has been extensively studied in order to obtain coatings with a high density of carboxylic acid (-COOH) groups, especially in the framework of biological applications [1]. Carboxylic groups are sensitive to pH changes of the solution. Therefore, it could be used in drug delivery systems to release a certain amount of a drug in an environment characterized by a specific pH value [2]. Plasma-polymerized acrylic acid coatings are expected to be beneficial for a wide range of applications. However, their implementations are hindered by their low functionality and irregularity [3]. Different studies have shown that COOH-rich surfaces can be successfully obtained by plasma polymerization of acrylic acid [1, 4, 5] but the regularity of films and the functionality are still not good enough. Thus the effect of CO₂ gas on the regularity and functionality of plasma deposited polyacrylic acid was studied in details in this contribution.

2. Experimental

The deposition experiments were achieved in a stainless steel reactor Ilmvac, Germany with volume of 50 dm³ with a pulsable radio-frequency (rf 13.56 MHz) generator with an automatic matching unit. For more details see ref [6]. The total flow rate (F) is adjusted to 34 g/h. The fixed plasma parameters were a duty cycle (DC) of 0.5, a pulse frequency of 1 kHz, an effective power of 50 W and the pressure was kept constant at 10 Pa. The studied molar fractions X_A of AA compared to CO₂ are: 75, and 100, where X_A is defined as

$$X_A = \frac{n_A}{n_{total}}$$

where n_A and n_{total} are the number of moles of AA and total number of moles in the mixture, respectively.

3. Results and Discussion

3.1. XPS measurements

XPS cannot be used directly to determine the number of the carboxyl acid group -COOH, therefore, a Trifluoroethanol derivatisation (TFE) labelling technique was used to differentiate between the functional groups -COOH and -COORCF₃ according to the protocol given in detail in Ref. [5, 7]. Trifluoroethanol is used to esterify the acid groups, but not the ester groups:



Thus, the acid group is labeled with fluorine which causes the -COOCH₂CF₃. This peak shifts to a higher binding energy compared to the other components of the C 1s peak. Through this, the fraction of -COOH within the -COOR peak can be obtained by curve fitting of the C 1s peak (Fig. 1).

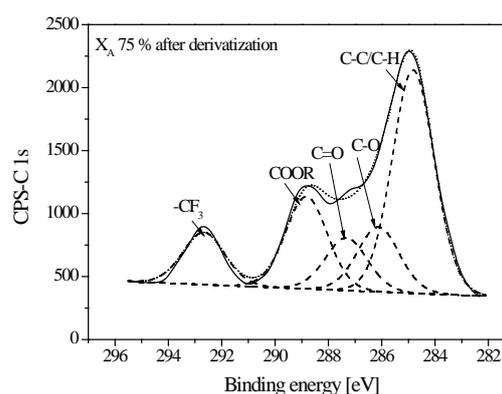


Fig. 1. C 1s peaks of the AA/CO₂ sample deposited on PE with molar ratio X_A = 75% after derivatization with TFE.

The concentration of -COOH groups was increased in the acrylic acid deposited polymer layer in presence of 25% of CO₂ gas by ca. 50% (Fig. 2).

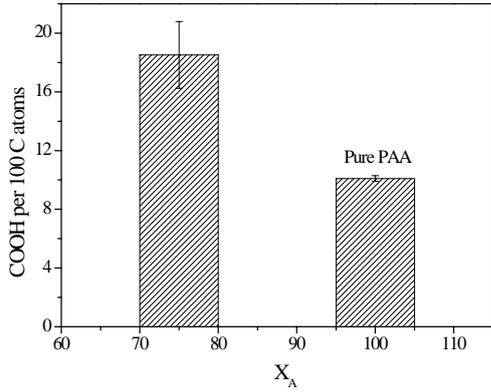


Fig. 2. Concentration of COOH groups per 100 carbon atoms for AA/CO₂ plasma deposited polymer films on PE.

3.2. FTIR spectroscopy

Fig. 3 represents the FTIR spectra of coatings deposited for AA/CO₂ ($X_A = 75\%$) compared to pure PAA ($X_A = 100\%$). Both spectra are quite similar. FTIR spectra of the deposited films show a very strong absorption band at $\sim 1710\text{ cm}^{-1}$ which can be assigned to C=O stretching vibrations of carboxylic acids. The FTIR spectra also contain a very broad absorption band in the region $3600 - 2400\text{ cm}^{-1}$, which can be attributed to OH stretching vibrations in carboxylic acids (Fig. 3) [8].

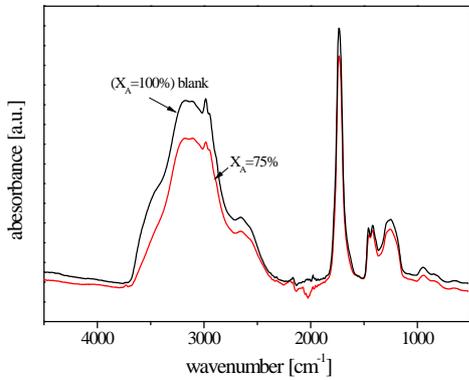


Fig. 3. FTIR spectra of AA/CO₂ plasma deposited polymer films on aluminum substrate for 100% and 75% PAA.

3.3. Broadband Dielectric spectroscopy (BDS)

A general overview about the dielectric relaxation behaviour of polymers can be found in textbooks [9, 10]. Fig. 4 give the dielectric loss for plasma PAA with ($X_A=100\%$) versus frequency and temperature in a 3D representation as example.

One relaxation process indicated by a peak in the dielectric loss is observed at low temperature which is called as β -relaxation. As expected it shifts to higher frequencies with increasing temperature. For higher temperatures the dielectric loss increases with frequency

and temperature without any indication of a further relaxation process. That increase of the dielectric loss is related to conduction phenomena related to the drift motion of charge carriers.

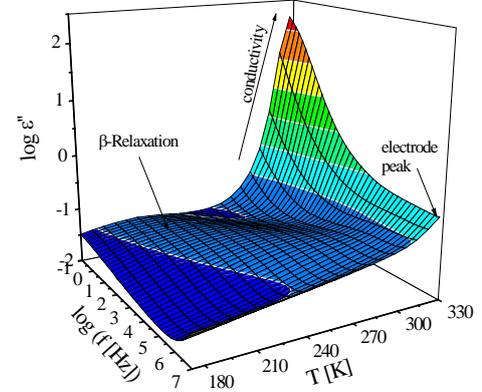


Fig. 4. Dielectric loss ε'' vs. frequency and temperature in a 3D plot for PAA samples with $X_A = 100\%$ representation as example.

In the case of AA/CO₂ β -relaxation is shifted to higher frequencies than for that pure PAA at the same temperature. This indicates structural changes of PAA in presence of CO₂ gas.

The data are analysed by fitting the HN-function to the data. The contribution of the electrodes is taken into as described in ref. [5]. Thus, the whole fit function reads as:

$$\varepsilon''(f) = \text{Im} \left\{ \frac{\Delta\varepsilon}{(1 + (if/f_0)^\beta)^\gamma} \right\} + A * f \quad (1)$$

where β and γ are fractional parameters ($0 < \beta \leq 1$ and $0 < \gamma \leq 1$) characterizing the shape of the relaxation time spectra, f_0 is a characteristic frequency related to f_p and A is a fitting parameter which is mainly due to τ_{Res} .

The temperature dependence of the relaxation rate $f_{p,\beta}$ of the β -relaxation is linear versus inverse temperature. Therefore, it can be described by the Arrhenius equation:

$$f_{p,\beta} = f_\infty \exp\left(-\frac{E_A}{k_B T}\right) \quad (2)$$

where f_∞ the pre-exponential factor and E_A is the activation energy. The estimated values of the activation energy are 66.1 kJ/mol and 55.9 kJ/mol for $X_A = 100\%$ (pure PAA) and $X_A = 75\%$ respectively. The values are in the order of magnitude of localized processes where the activation energy for $X_A = 100\%$ is essential higher than that of $X_A = 75\%$. The reason for the different behaviour is unclear up to now and requires additional investigations.

4. Conclusion

Thin PAA films were deposited by pulsed plasma polymerization on different substrates (organic and inorganic). The structure-property relationships of acrylic acid/CO₂ polymers were studied by various techniques and probes.

It was found that in presence of CO₂ gas in the precursor mixture, a polymer network is obtained with an increasing abundance of branched groups. Those groups are accompanied by a decrease of activation energy and cross-linking. However, a structure of polyacrylic acid with higher concentration of COOH groups than that for pure one was obtained.

5. References

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